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Oil Stains*

By H. R. HIRST, M.Sc., F.I.C., M. I. Chem. E.

The effects of exposure to light, of scouring and dyeing, and of steaming and storing, on wool stained with various types of oil are discussed in this article.

OILS are the usual lubricants used in the textile industry, and inadvertent contact of fresh or soiled oil with fabrics frequently leads to the formation of stains. Such oil stains may exist as colored oil films, which are defects in themselves, or may act as causes of irregular dyeing. Mineral oils are liable to cause discoloration on white goods. They can also give rise to various types of unevenness or marks by affecting the rate of absorption of fibers for dyes, and hence their levelness. Considerable attention has recently been given to oils used for lubricating textile knitting machines [*i.e.*, so-called white or stainless oils—ED. T. M.].

The general impression that oils merely act as resists has to be considerably modified in the light of recent observations. Oils can produce dark or light colored patches, depending on certain conditions.

Textile machinery is now generally lubricated with oils wholly or largely composed of hydrocarbon oils derived from crude petroleum; such oils spotted on to fabrics rapidly turn yellow or brown after comparatively short exposure to air and light, the amount of discoloration on exposure depending on the purity of the oil.

Mineral oils, whether obtained by distilling crude petroleum or shale, consist of mixtures of hydrocarbons the exact composition of which is still little known. Treatment with sulphuric acid, followed by washing with caustic soda, and in some cases further purification by filtering through fuller's earth, gives oils which are paler in color (even water-white) than the crude oils, and which are free from the objectionable gumming and discoloration on exposure to air and light. These highly purified oils are not affected by light and air, and fabrics oiled with them do not turn brown or yellow on exposure. They are known as non-staining oils. Medicinal paraffin B.P. is a perfect example of non-staining oil, and is probably composed entirely of saturated hydrocarbons and free from bituminous and resinous compounds.

If an ordinary mineral lubricating oil (*e.g.*, a Scotch 885/90 or American spindle oil D, Table III.) be exposed in the fadeometer in a quartz tube, the blue fluorescence in ultra-violet radiation gradually disappears, and a brown precipitate forms which can be separated fairly completely from the oils by its insolubility in petroleum ether, whereby the oil is freed from resins, and also the fluorescence in the oil changes to white. After 175 hours' exposure in the fadeometer, American spindle oil D gave 0.8% insoluble in petroleum ether and Scotch 885/90 gave 0.06% insoluble, but the period of maximum change had not been reached.

Mineral oils contained in Petrie dishes and exposed in the fadeometer, if of the non-staining type, do not change, whereas staining oils rapidly darken, and in 30-60 hours become viscous, and a yellow or brown precipitate is visible. A sample of "C" spindle oil gave a tarry mass, insoluble in petroleum ether, of which a portion was insoluble in ethyl ether. This was almost completely dissolved by benzene and trichloroethylene, and the final residue was soluble successively in alcohol and acetone. The whole residue is soluble in cyclohexanol. Oil 250 L (Stemco), exposed in a Petrie dish, left on residue. An American oil "E" left 2.07% residue insoluble in petroleum ether. This residue readily wets out with water.

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* Journal Society of Dyers and Colourists.

Fatty oils exposed in the same manner behave differently; oleic acid (purified) and cotton-seed oil, which originally show blue fluorescence in the ultra-violet, show yellow fluorscence after exposure in the fadeometer for twelve days. After six weeks' exposure the fluorescence has disappeared. Wool oiled with cotton-seed oil and stored for four months in a dark room shows a similar yellow fluorescence in the ultra-violet testing cabinet.

Stains on Scoured White Worsted

Instead of using Petrie dishes, it is, however, more convenient and useful to observe the appearance of oils spotted on to white scoured worsted cloth, and then exposed to light. Patterns were exposed at Clifford, Yorkshire, behind Vita glass for 15 days in June, 1930, and gave the same changes in color as exposure to the fadeometer for 23½ hours. A number of oils which were stated to be spotless, and various fatty oils and varities of American mineral oils, were tested.

Table I.—Effect of Exposure on Oil Stains

Name of Oil	Source	Appearance After Exposure
Oil "F"	Anglo-American Oil Co.	Very faint yellow
Oil "A"	Anglo-American Oil Co.	Yellow
Oil "E"	Anglo-American Oil Co.	Yellow
Marcol	Stemco Ltd.	Nil
Half white oil	Stemco Ltd.	Very faint
"D" spindle oil	Anglo-American Oil Co.	Strong yellow
"B" pale oil	Anglo-American Oil Co.	Strong yellow
"250L" white oil	Stemco Ltd.	Nil
"C" spindle oil	Anglo-American Oil Co.	Yellow
Bloomless white mineral oil	B. Vickers and Sons Ltd.	Nil
Spotless "A.B.W."	B. Vickers and Sons Ltd	Nil
Spindle oil	B. Vickers and Sons Ltd.	Yellow
Loom oil	B. Vickers and Sons Ltd.	Yellow
Spotless "I.A.W."	B. Vickers and Sons Ltd.	Very faint
Oil "2130"	B. Vickers and Sons Ltd.	Faint yellow
Latherine	B. Vickers and Sons Ltd.	Very faint
Malaga olive oil	.....	Nil
Pale Scotch oil—		
"890/95"	.....	Deep orange
"865/70"	.....	Deep orange
Liquid paraffin B.P.	Reynolds and Branson	Nil
Purified oleic acid	Laboratory preparation.	Very faint yellow
Pale distilled oleine	.....	Faint yellow
Distilled tallow oleine	.....	Pale yellow

The appearance of the oils exposed to daylight was the same as when exposed in the fadeometer. If spotted on cloth and exposed in the fadeometer for a period of 30 hours, the oils give a maximum darkening.

Mineral oils were exposed to daylight in August, 1931. One day of diffused daylight gave a distinct change from the yellow of the original oil to a brown color. Samples of Rumanian, Persian, and Russian oils were completely changed to brown with eight days' exposure in August, 1931, three days of which were bright sunlight, the remainder diffused light.

The Rumanian and Persian oils were much changed, but the Russian oil was only slightly discolored. Russian oil is said to contain hydrocarbons of the naphthene series, these being cyclic compounds which do not combine directly with bromine. Naphthenes are present only in small quantities in American and other petroleums, their place being taken by olefines, which accounts for differences in behavior on exposure. Only single authentic samples of these oils were available; in the author's opinion they are worth further study.

It is probably rare for mineral oil stains to reach their maximum staining during the periods of exposure to light to which yarn, cloth, or hosiery is subjected in practice, but, nevertheless, very dark-colored stains have been observed, and for the purpose of testing oils it is advisable to expose them for the period of maximum change. Therefore, in testing oils spotted on white worsted cloth, they were exposed for 30 hours in the fadeometer; longer exposure tends to bleach the stains. Comparison of oiled yarn stored under commercial conditions and exposed in the fadeometer is being carried out.

Staining Test by Fluorescence

On comparing the staining power of mineral oils with their fluorescence in ultra-violet rays, it was found that there is apparently some relation between the appearance of the fluorescence and the amount of staining produced on exposure to atmospheric influences. If the ultra-violet rays be allowed to fall vertically on to an oil in a quartz tube, one of two different effects is visible—

1. A brilliant glow on the surface of the oil (e.g., sp. gr. 0.885 American).
2. The oil is luminous to a considerable depth (e.g., vacuum oil 2960).

If oils of type 1 are diluted with medicinal paraffin B.P., using one part of oil type 1 to 2000 parts or less of medicinal paraffin B.P., they change to oils of type 2, and the change is reasonably sharp—i.e., there is a clear distinction between dilution of 1000: 1 and 2000: 1. This method can be used as a qualitative test or as a quantitative method within limits. (Petroleum ether can replace medicinal paraffin.)

Instead of using a purified mineral oil as a standard for such tests, an aqueous solution of quinine sulphate and Indigosol O can be used to match any blue or blue-green fluorescent oil when diluted as above, or a purified oil. Indigosol O gives a deep violet and quinine sulphate a greenish-blue fluorescence; mixtures of the two can therefore be adjusted to match the blue or blue-green fluorescence of mineral oils, and should be used in neutral or faintly acid solution.

Staining by Fatty Oil Mixtures

Samples of animal and nut oils, and mixtures of the same with purified mineral oils, were tested in the fadeometer. Mixtures of staining oils with some fatty oils were prepared in order to determine whether the presence of fatty oils will prevent staining and assist in complete scouring out, even if staining of the mineral oil has taken place. Cloth spotted with the following oils was exposed for 40 hours in the fadeometer, and scoured with 0.2% soap and 0.1% alkali solution at 45° C. for 20 mins.

American mineral oil, sp. gr. 0.885 (3 parts), oleine (1 part)—Gave no stain after scouring, but stained after dyeing.

American mineral oil, sp. gr. 0.885 (2 parts), olive oil (1 part)—Was stained after scouring, and stained after dyeing.

Tests show that mineral oils spotted on to fabrics oiled with olive oil or oleine will produce permanent stains under some conditions.

The purified mineral oils commercially available are of low viscosity, and suitable only for light machinery such as knitting frames; if more viscose oils are required, additions of animal or nut oils must be made. Tests of some commercial samples of these mixtures did not give a very satisfactory result in being stainless, although a few exceptions were noted. There should not be any difficulty in producing stainless oils, or at any rate oils which give such slight staining that they are readily scoured out. Batches of oil can now be tested by means of the fadeometer and subsequent scouring and dyeing, so that reasonably good commercial oils can be blended.

Effects of Dyeing on Oil Stains

Cloths spotted with mineral oils of the staining type were either thoroughly scoured with soap and water until the stain was invisible or hardly visible if heated with boiling solvents—e.g., ether or benzene. But when dyed with acid dyes, the cloth shows a much fuller shade on the place where the oil was originally spotted. This is not due to the effect of the oil stain modifying the dye color, but is actually due to greater depth of shade.

The cause has been studied in some detail. (It was thought that the effect might serve as a method for testing the scouring power of different soaps, by observing the different depths of color after dyeing. Several trials indicated that there is some difference, but hardly enough to be used as a test.) Differential light action on the fabric is ruled out because the depth of color on the stain is far greater than that of the unoiled cloth exposed to light. Cloths spotted with oil and allowed to stand at ordinary temperatures or in an oven at 100° C. were compared with spots exposed to the fadeometer for the same time. The former gives no stains on dyeing. Hence this staining is not due to heat.

Sometimes mineral-oil stains give dark stains on dyed fabrics, when, according to expectations, they should have given light-colored resist marks, and this has always been a source of surprise. It was noticed that if oil stains are only exposed for a short time to light (up to four hours in the fadeometer), they give light-colored stains. It appears as though the light and air action must penetrate the whole oil layer in order to give dark dye stains; thus two types of stains are possible. A further observation was that, after scouring and dyeing, these stained parts wet out immediately when placed on the surface of water. Large patterns treated with oil in benzene solution and exposed to the sun were compared with similar cloth without oil, both being well scoured in soap and hot water. When tested by the funnel test for waterproofing, using 200 c.c. of water, the oiled cloth commenced to drip in 45 secs., and dripping was complete in 5 mins. 15 secs., whereas the unoiled cloth commenced to drip in 190 secs. and required 30 mins. for completion. Thus, exposed oiled cloth is less waterproof, the layer of "oxidized" oil facilitating wetting-out, and this appears to be the reason why oiled wool absorbs more dye. The more intimate contact with the dye solution results in a greater exchange of liquor through the fabric, and possibly greater action of alkali on the wool during scouring, which would increase the affinity of the wool for dyes.

Basic colors dye the oiled patch fuller in shade at first, but almost level up on boiling. It is somewhat unusual for basic dyes to give the same result as acid dyes on wool. This behavior shows that the cause is other than the usual atmospheric effects causing different dyeing affinity. Easily levelling acid dyes behave in a similar manner, but the difference in shade of the oiled and unoiled portions is generally of the reverse order.

Material cleaned with ether or benzene dyes dark on the oil spot. The effect, therefore, is not due entirely to absorption of alkali by the wool, although this is a factor. Material which has been given a heavy scour to remove the oil, dyes much darker, as a whole, than when an ordinary light scour has been given.

Various scouring agents were used. A solution of 1% soap and 0.05% soda ash, at 40° C., worked for 15 mins. and wrung out five times, was found to give excellent results, as also did a scour using 0.2% soap and 0.1% soda ash at 45°C. for 20 mins. with constant agitation. This latter method is very satisfactory and simple. Scouring tests using 0.3% solution of Igepon A did not prove to be quite so satisfactory.

Similar dark-colored markings on dyed hosiery have been traced to mineral-oil stains.

In order to ascertain if the effect of the oil on the wool was due to the removal of fats held internally, wool extracted for three days with boiling alcohol was used. The affinity of the wools was definitely altered, its affinity for acid dyes being increased, and for basic dyes decreased. When spotted with oil, exposed, scoured, and dyed, the extracted wool gave exactly the same effect as untreated wolo. The effect, therefore, is not due to the solvent action of oil on wool fat in the fiber. Wool spotted with mineral oil and heated to various temperatures up to and including 100° C. for the same period as exposure to light, does not give a dark color on scouring and dyeing. Thus the effect is not caused by heat alone. Wool stained with mineral oil and stored in the dark with access to air gives a similar result to exposure in the fadeometer.

The wetting-out effect of the exposed oil is considerable. Addition of Leonil S to the scouring bath or the dyebath does not make any difference; other similar agents were tested without result. Thus these substances are useless as preventives of this type of stain.

Effects of Impurities in Oils

The presence of finely divided metals in lubricating oils is another source of trouble. Tests have shown that dirty spindle or loom oils are difficult to remove by scouring, and are apt to leave spots or stripes of dirt containing metals, particularly iron. This gives rise to light or almost colorless stains when dyed with Coomassie Navy Blue;

mordant dyes which are sensitive to iron give their own characteristic effects. In another case fabrics bleached with hydrogen peroxide were rotted where the iron stains were present, and in any case the residual iron was converted into brown stains of ferric oxide.

Unless the oils are suitably refined for the purpose, attempts to obtain cheap lubricating oils, and to replace fatty oils by hydrocarbon oils for combining and blending, result in dangers of a special kind, which will tend to become worse the longer the material is stored before scouring, or is exposed to light during storage.

Experiments show that there is no special difficulty in scouring purified mineral oils out of woolen fabrics, but oils containing compounds which tend to polymerize or change into resinous or asphaltic substances should be avoided at all costs, on account of their liability to cause stains.

Effects of Storing and Steaming

Fatty oils stain more readily when stored in the dark than when exposed to light. It has been shown that light bleaches these stains as rapidly as they are formed by atmospheric influences. At present the method for investigating the staining of fatty oils is by storing oiled material for a long period, and is therefore useless as a routine test. The tests given below require four months' storing for complete development of the colors.

Steaming oiled patterns has been tried tentatively as a test. It was thought that probably the action of steam and air would give results similar to ageing in the dark, and tests were made on a number of typical oils, spotted on to white worsted cloth. The method for making the test is to blow a slow stream of air through boiling water in a steamer, which may be a wide-mouthed flask or a large metal steamer. The patterns are hung in the current of steam and air for the requisite time, dried and examined. The results of one test are given in Table II.

In Table II seal oil was used to give a visual standard to judge when "oxidation" was well advanced. The appearance in ultra-violet is given, as it is useful as a guide to the examination of oil stains, etc. The appearance after steaming for one hour at 100° C. with admixture of air is given, because steaming of yarn is not an uncommon practice, and also steaming is used as a test for staining of oils, and a comparison with the storage results is of value. Generally, the results of the two methods agree, more particularly in depth of color, but vary slightly in shade. Mineral oils of the ordinary type give dark stains on wool, when crabbed, scoured, dyed, and finished, whereas stainless mineral oils or liquid paraffin give light stains under similar conditions. When applied in trichlorethylene or benzene solution the tendency is to give light-colored marks with ordinary mineral oils and dark stains with purified oils. There is apparently no rule as to the type of stain produced, but a stain is invariably produced. When, however, scouring precedes crabbing, the stains are in some cases absent and in other cases only faint, because the oil has been scoured out before steam is applied.

Oxidation of Olive Oil

The effect of a mixture of steam and air on tops oiled with Malaga olive oil was investigated. Steaming in the presence of air causes a certain amount of oxidation; the figures vary considerably, and show two distinct rises and falls in the ratios of oxidized oils (after 2 hours 18.15% fatty acids oxidized, after 3 hours 12.91%, after 8 hours 16.37%). It must not be overlooked that this "oxidation" is taking place in a short period of time. Oxidation on storage is much more regular, and shows a gradual increase up to 21.27% after 343 days.

Color changes obtained by steaming are similar to those obtained by storage; it would thus appear that color

(Continued on page 293)

Table II.—Effects of Storing, Steaming, Scouring and Dyeing

	Appearance in Ultra-violet Before Exposure	Appearance in Ultra-violet After Steaming and Storing 4 Months	Appearance in Ultra-violet After Storing 4 Months	Appearance in Daylight After Steaming	Appearance in Daylight After 4 Months' Storage	Appearance in Daylight Before Exposure, Freshly Spotted	Appearance in Daylight After Scouring and Dyeing
Oleic acid purified..	Nil	Pale yellow	White	V. pale yellow	Pale yellow	Nil	Visibly darker
Oleic acid pure (Kahlbaum).....	Pale yellow	Pale yellow	White	V. pale yellow	Pale yellow		Visibly darker
75% oleic acid.....	Blue	Pale yellow	White	V. pale yellow	Pale yellow	Nil	Visibly darker
Pale Dutch distilled oleine.....	Pale yellow	Pale yellow	White	V. pale yellow	Pale yellow	Nil	Visibly darker
Pale distilled tallow oleine.....	Nil	Pale yellow	White	V. pale yellow	Yellow	Nil	Visibly darker
95% distilled oleine.	Yellow	Nil	White	Pale yellow			Visibly darker
Bloomless white mineral oil.....	Nil	Nil	White	V. pale yellow	V. pale yellow	Faint brown	Visibly darker
Olive oil Malaga...	Pale brown	V. pale bright yellow	Pale yellow	V. pale yellow			Very slightly paler
Arachis oil.....	Brown	Strong bright yellow	Pale yellow	Pale brown	Pale brown	Nil	Visibly lighter color
Cotton-seed oil....	Blue	V. pale yellow	Pale yellow	V. pale yellow		Nil	Undyed patch
"Worsted oil".....	Pale brown	V. pale yellow	Pale yellow	Pale brown	Strong yellow	Nil	Visibly darker
Brown cloth oil....	Yellow	V. pale yellow	White	Pale brown		Nil	Visibly darker
Another sample....	Nil	Strong bright yellow	White	Pale brown	Pale yellow		Visibly darker
70% wool grease oleine.....	White	Medium bright yellow	Bright yellow	Strong yellow	Pale yellow	Pale brown	Visibly darker
Wool oil.....	Blue	Strong golden yellow	Bright yellow	Strong yellow	Pale yellow	Pale brown	Visibly darker
Seal oil.....	Strong yellow	Fairly bright yellow	Golden yellow	Very strong brown	Yellow	Pale brown	Visibly darker
Turkey-red oil.....	Pale yellow		—	—	Very strong brown	Yellow	Visibly lighter color
Olive-oil substitute.	White	Pale yellow	Pale yellow	Pale yellow	Yellow Pale yellow	Nil Nil	Undyed patch

NOTES—Pale yellow and pale brown mean same depth of color but different hue. Brown is actually yellowish-brown. The four months' storage was carried out in a dark room having a rather moist atmosphere, similar to the conditions under which tops and yarns are stored.

Proceedings of the American Association of Textile Chemists and Colorists

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CALENDAR OF COMING EVENTS

Meeting Northern New England Section, May 7.

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Meeting New York Section, May 27.

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Council and Research Committee Meetings

May 6, 1932—New York City.

June 3, 1932—Boston, Mass.

* * *

Meeting Southeastern Section, April 30.

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Outing Mid-West Section in June.

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SPRING MEETING, MID-WEST SECTION

The Spring meeting of the Mid-west Section of the American Association of Textile Chemists and Colorists was held on Saturday evening, February 27, 1932, at the Bismarck Hotel, Chicago, Illinois. The meeting was preceded by a dinner. About 60 were present at the meeting.

Following the routine business of the meeting informal group discussions were held.

The next meeting will be in the form of a summer outing to be held in June.

Respectfully submitted,
William Bergh, Jr.,
Secretary.

MARCH MEETING, RHODE ISLAND SECTION

The March meeting of the Rhode Island Section of the American Association of Textile Chemists and Colorists was held on Friday evening, March 11th, 1932, in the rooms of the Providence Engineering Society.

At the request of the Chairman, Mr. Heyward F. Lawton, the President of the Association, Mr. P. J. Wood, who, together with several members of the Council and Research Committee was present at this meeting, said a few words to the members.

Two interesting papers were given. The first was by Mr. G. V. Caesar of the Stein Hall Company and was entitled "Some Properties of Starch and Dextrine." The second was given by Mr. James Shanks of the Lorraine Manufacturing Company and was entitled "Rayon Warp Sizing."

Approximately ninety-seven members were present.

Respectfully submitted,
Brian Wainwright,
Secretary.

Proceedings of the American Association of Textile Chemists and Colorists

Some Properties of Starch and Dextrine*

By GEO. V. CAESAR
Laboratory Director, Stein, Hall & Co., Inc.

I HAVE chosen as the topic of my address a brief discussion of some of the properties of starch and its derivatives. I shall not try to tell you how to use starches and dextrines—in this gathering that would be about as useful as our diplomatic notes to Japan. My purpose, rather, is to explain certain fundamental properties in the light of recent studies.

Nature stores in the form of little packages the complex carbohydrates chemically known as starch. These little packages take the form of granules of various sizes and shapes characteristic of each plant, varying from the large oblong granules of Potato, Canna, etc. to the tiny irregular granules of Rice; and for each species there is usually a marked variation in the size of granules.

I have used the term "packages" to describe these starch granules, for in the light of the latest research this description most perfectly applies. Heretofore a starch granule was visualized as a little sack or bag, consisting of a flexible envelope of insoluble starch, enclosing a soluble interior.

Now, largely through the work of Dr. Taylor at Columbia University, with whom, by the way, we are associated, it has been proved that although starch does indeed consist of two constituents, *every part* of the starch granule contains a definite ratio of these soluble and insoluble portions.[1] This heterogeneous mixture is tightly packed or compressed into the little packages which we view under the microscope as granules large and small. The compression is least at the center of the granule and highest near the surface.

For the insoluble portion of the granule I shall employ the term "alpha amylose" and for the soluble portion "beta amylose." The proportion of alpha to beta is approximately as follows:

For Corn and Tapioca	15:85
For Rice	12:88
For Potato	3:97
For Wheat	24:76

The above ratios were determined by Dr. Taylor by electrophoresis of mobile pastes in which all traces of the original swollen cell structure had been destroyed by a special pre-treatment. The alpha amylose migrated slowly to the positive electrode and the beta remained in a clear solution from which it was later precipitated by alcohol and dried and weighed. Perhaps the most interesting fact uncovered by these isolations of the two principal constituents of starch is the extremely low viscosities of the separated or combined amyloses: A one per cent concentration only slightly exceeds the viscosity of water.[2] Bear in mind that the true proportions of these amyloses become available for separation by electrophoresis only *after complete cell rupture;* if any unruptured little swollen package (which I shall term cells) remain in such a paste, then the proportion of alpha will be apparently higher than normal, and the viscosity will be higher too. The less the degree of rupture or cell destruction in any given paste, the higher the viscosity or "body" of that paste. Thus, the body of any given concentration of a starch in water, after cooking, depends principally upon what has happened to these little packages or granules after swelling.

Now by means of an instrument which we have recently designed, we are able to obtain a graphical "picture" of the plastic properties, or the consistency of starch pastes, as a function of the degree of mechanical agitation and time and temperature of cooking under uniform conditions. We have termed this instrument the "Consistometer." It has proved to be very precise—the measurements being recorded in electrical units — and much more satisfactory and instructive in many respects than the ordinary flow-type of viscosimeter, which, for starches, is limited to very low concentrations and susceptible to gross errors because of the difficulty of obtaining consistently uniform treatment of the pastes prior to viscosity measurements. For example, one operator may stir a paste a trifle longer or more vigorously than another and wide variations in time of flow may result. The Consistometer affords a study of consistency under uniform agitation.

In Figure No. 1 are plotted typical curves showing the consistency history of 20 per cent concentrations of Tapioca, Corn, Potato and Wheat. The numbers on the vertical scale represent electrical units, on the horizontal scale are water-jacket temperatures in degrees F. Since

* Presented at March Meeting, Rhode Island Section.

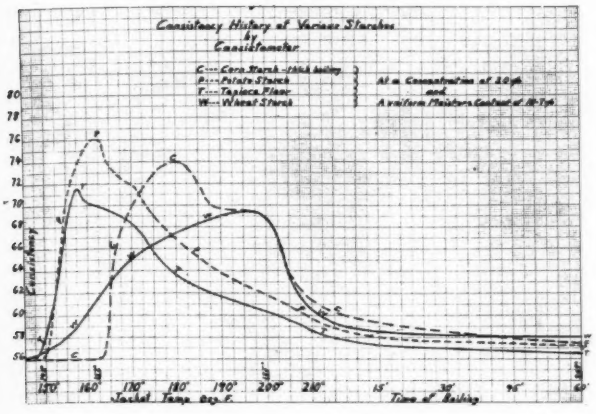

Figure 1

the water-jacket is well lagged and the water (of constant volume) is electrically heated under a constant voltage, its temperature rise is very uniform. Actual temperatures of the pastes, therefore, bear a constant ratio to the recorded water-jacket temperatures. Certain of the more important "paste temperatures" are recorded on the chart in small figures.

Beginning with the curve for Tapioca, we note that a steep rise in body occurs at a paste temperature of about 140° F.—that a maximum body or "peak" is attained at 147° F., after which the curve falls more or less rapidly towards the boiling point and gradually approaches a minimum, beyond which further heating and agitating are of little or no effect. Potato behaves similarly to Tapioca but is heavier. (Compared weight for weight, the gap between the curves for Tapioca and Potato would disappear, owing to the inherently high moisture content of Potato starch. The curves of Figure No. 1 represent equal solids.) For Corn (thick boiling) no appreciable thickening occurs until its paste temperature reaches 152° F., after which the curve representing consistency or body again arises steeply, but exhibits a wholly different "peak" from Tapioca and Potato, being more rounded and less hurried in its descent. And now note carefully the form of the Wheat curve! It is quite unlike the others. Thickening begins at the temperature of Tapioca and Potato, and the curve rises slowly in a smooth ascent to a jacket temperature of 200° (185° paste temperature). Here it merges with the Corn curve and falls steeply; but after fifteen minutes boiling it attains a constant body.

Let me explain what these curves signify: The upslope reveals the initial swelling of the granules and the peaks are thus a comparative measure of swelling power. The reverse slope of the curves shows the ever increasing effect of cell-rupture; and near the peak, before the downward tendency is well under way, this rupturing process for a time is more or less in equilibrium with the delayed swelling of the smallest and most resistant of the original granules. In the case of Wheat Starch, however, the cells (partly perhaps by virtue of their higher alpha content) remain exceedingly resistant to rupture until a paste temperature of about 185°. F. is attained. Above 185° a large proportion of the cells rupture almost simultaneously under the very severe agitation of the Consistometer; but at the end of the curve many unruptured cells are still present. The consistency curve for Wheat Starch thus proves exceptional ability to maintain a heavy body under severe conditions of heat and agitation. And this, of course, is of practical interest.

As these consistency curves indicate, swelling or gelatinization, although rapid above a certain temperature, is by no means an instantaneous process. In other words, we cannot refer to a definite "gelatinization temperature" for Corn, Tapioca, etc., unless we mean that temperature at which all of the granules have swollen, i.e., complete gelatinization. The swelling process takes place over a *range of temperature.*

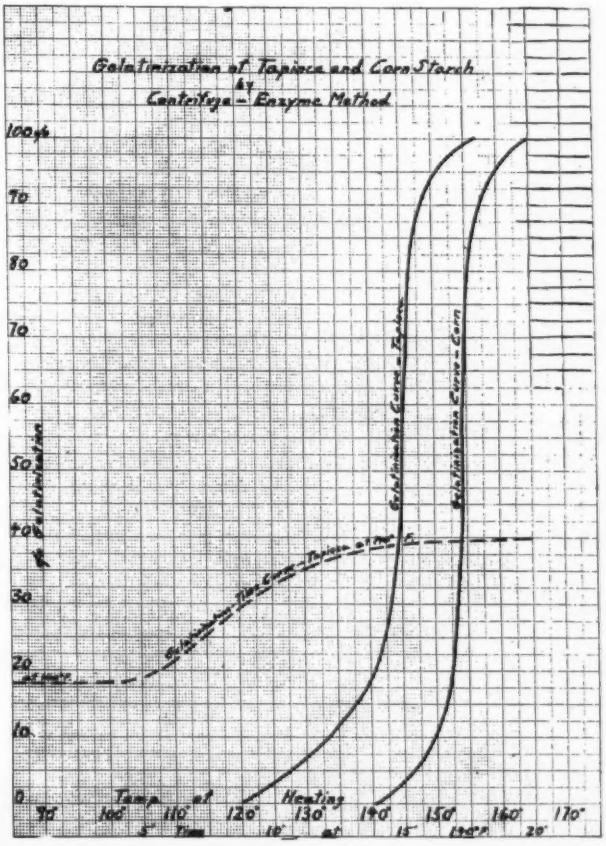

Figure 2

Figure No. 2 shows the gelatinization temperature for Tapioca and Corn. For the sample of high grade Tapioca, no appreciable swelling occurs below 120° F. At this temperature certain of the larger granules commence to swell, the curve rising slowly to 140° F. About 20 per cent of the granules will have swollen after five minutes at this temperature. Longer periods of heating will cause further swelling (as shown in the dotted curve) but not to exceed a maximum (at 140° F.) of about 40 per cent. Above 140° F. the swelling increases very rapidly and is practically complete at 155° F. Comparing Corn at the same rate of heating, swelling does not begin below 140° F., reaches a value of 10 per cent at 150° F. and then rises very rapidly to completion at 165° F. Thus, we find an average spread of about 10° F. between the gelatinization curves of Tapioca and Corn.

It is extraordinary how much mechanical energy is required to rupture these gelatinized or swollen granules. Even after long periods of cooking and stirring in the Consistometer, careful staining with Iodine or Gentian Violet reveals under the microscope distorted but unbroken cells, the number and distortion of which vary with the kind of starch used. In Potato, also in Tapioca, the degree of rupture will be pronounced, but numerous striations indicate that the beta amylose is still quantitatively unavailable; in Wheat the degree of rupture will be comparatively slight. Dr. Taylor states[2] that Corn Starch pastes, boiled in an autoclave at fifteen pounds above atmospheric pressure, still show a large number of swollen cells, and that even after passing a starch paste through an homogenizer, a microscopic study showed marked striations, the alpha amylose content yielding the fictitiously high value of 62.5 per cent as against 15 per cent for the completely ruptured starch. Thus, by mechanical treatment of pure starch pastes, it is very difficult—perhaps impossible—to reduce the body or viscosity below a certain value. In its early stages, rupturing is relatively rapid but soon becomes slower, barring hydrolytic degeneration of which I shall speak further.

So much for pure starch pastes. I trust that I have made clear to you that it is primarily the physical state of this conglomerate of amyloses and swollen cells, in various degrees of rupture, upon which we must depend for the working properties of starches.

I shall now treat briefly of the more or less soluble derivatives of starch. Although the exact structural formula of the amyloses is still wanting, it is rather generally conceded that they are polymers of alpha glucose, the glucose rings connected by oxygen bindings. The dextrinization of starch is exceedingly complex, and it must be confessed that the majority of technical investigations of this subject have not clarified it. A complicated nomenclature has evolved—amylodextrin, erythrodextrin, achroodextrin, etc. It is improbable that these are definite compounds; no doubt they represent complex mixtures of hydrolytically degenerated and dehydrated amyloses. Acid treatment to produce so-called "soluble starch" involves hydrolytic degeneration, or a splitting of the glucose chains at the oxygen binding, the degree of which will depend upon the severity of the treatment. Heat treatment (torrefaction or roasting) involves essentially a dehydration of the glucose chain combined with a variable amount of hydrolytic splitting in the early stages of the process.

The "British Gums" with which you are familiar are produced essentially by roasting. They can be obtained in a wide range of solubility and body. Generally speaking, the body of a gum will vary inversely as the solubility, the lower soluble gums exhibiting "starchy characteristics." By "starchy characteristics" I refer to the presence of abundant swollen granules or cells in a paste of the gum and water. These cells are far more fragile, however, and easily ruptured than are those in pure starch pastes. In the higher solubility range of British gums the number of cells is low, and consequently the pastes are clearer and more fluid. In Vat color printing there seems to be a certain trend, for the moment, in favor of the heavy starchy gums for large designs; but from a technical point of view it would seem that the desired effects might be more simply and surely attained through the addition by the color-mixer of the required proportions of pure starch to soluble British gum.

I trust that I have been able to sketch you at least a reasonably clear picture of starch and dextrin. I have tried particularly to emphasize the importance of heating and agitation, since the usefulness of starch and its derivatives depends largely upon properties in water.

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1. *Ind. & Eng. Chem.* Vol. 18, No. 7, p. 713 (1926).
2. *J. Am. Chem. Soc.* 51, 294 (1929).
3. W. H. Haworth—"Ring Structure in the Holosides"—Dixieme Conference de L'Union Internationale de Chimie (Rapports sur les Hydrates de Carbone).

Proceedings of the American Association of Textile Chemists and Colorists

Rayon Warp Sizing*

By **JAMES SHANKS**
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IT IS an entirely new experience for me to address a group of men of this kind. Some I have met as salesmen and some I have not seen for several years. I did not prepare a paper to read but just brought a few notes about rayon, celanese and other acetate yarns, from the time they are received at the plant, until they reach the looms.

When a shipment of rayon yarn is received it is examined very closely, as the rayon manufacturers change their productions continuously and we are asked to keep these productions separate, otherwise, when it gets to the dyeing, variations occur, something you don't want. Of course, once in a while someone slips up.

When the yarn is warped it is examined for streaks. Quite often it softens or swells on warping, causing considerable streakiness. This streakiness shows up in weaving and again in the finishing room. The warping is done in different ways using either the silk warper or the cotton warper. It was found that equal results are obtained either way, depending on equipment.

At the present time about every type of size on the market is available. The majority of it has a gelatin or glue base. At any rate, the majority of those which were tested are glue or gelatin. In my opinion, the gelatin size makes the best woven goods. Softener can be put in so that the yarn looks good and runs good. At different times sizes containing starches, dextrin, glue and gelatinized natural gums have all been tried. They all come along at one time or another.

When cooking up the size, it is usually kept in an enclosed kettle, and indirect heating is used, and too much agitation is avoided after heating. The size is put in several containers so that it is not agitated to any great extent. Too much agitation tends to draw up the softener in the size so that it floats on the top. The tendency of the softener to float to the top causes spots which go right through to the finishing.

Gelatin shipments sometimes run good, then again shipments come which have foreign matter in them. This foreign matter will float to the top of the size, and it must be skimmed off, or removed in some way, to keep out of trouble.

In the dressing of these warps, a size is used depending on the goods being made. Just enough size is used so that it will hold it. A light size is used for 44 picks; for 58, 72, 90 or 96 picks the size is increased proportionately—the higher the pick the heavier the size. It is on the low-pick material that the most trouble is encountered. Sometimes when this gets out in the plant it is found to be full of tear marks or birds' eyes, and it can't be sold and it comes back to the plant.

All types of slashers are used, among them the so-called silk type and converted cotton type slasher. The silk slasher, such as the Johnson or Van Vlaanderen, is about as good as any. The surface speed is from six to thirty yards a minute. While very good results are obtained at six yards a minute, due to present business conditions, it is necessary to use higher speeds, running up to twenty, twenty-one or twenty-two yards surface speed. Low pressure steam is used for drying. By actual test, the temperature on the outside of the cans is from 175° F. to 190° F. Yarns dry well at these temperatures.

Regulation stretch must be applied on each type of rayon yarn. On the imported yarns it is impossible to get over 2% to 3% stretch. On domestic yarns, for example Viscose process, 10% to 14% stretch is obtained. The warps are run accordingly, to get the most stretch for best weaving results.

Several tests were made to find out actually, how much size remained on the yarn after dressing. A 15-cut warp was tested and 4% to 4½% size was found in the yarn, that is, added weight.

Many different kinds of softeners are used, sulphonated castor oils, sulphonated olive oils, sulphonated tallows and mineral oils, some having a sulphonated base and cocoanut oil. A sulphonated base and 55% Cochin makes a good softener. It is necessary to be very careful on softening the goods. If, for any reason, a hard warp is obtained, the goods cannot be sold. Of course, efforts are made to eliminate this sort of thing. One thing is important—the warps should not be stopped while dressing. If they are, hard places are produced where they stopped in the quetsch.

Next, take the water in which the size is mixed. If a little hard soda ash or perborate of soda is added to soften it. Quite often the water is hard and, from time

*Presented at March Meeting, Rhode Island Section.

to time, lime soaps form on the top, and this goes straight through to the looms unless removed.

There are the three-can system of drying, five-can, and single can or one large can. On the five-can system, faster drying speed is obtained than on the smaller type machines, either the three-can or the single can.

Before being thrown, the filling yarn has to be treated in order to retain its twist, so that it will be soft enough not to break down the warp, thus causing tear marks. The yarn is most always received in skeins of 10-pound bundles. A solution is made, usually using solutized wax or gelatin, oil and tint. The skeins are immersed five to fifteen minutes, removed, extracted and dried. They are then spooled and treated with steam to set the twist, then quilled and put on cops. At different times too much "dope," as it is called, and which is just gelatin or size, is deposited on the yarn. If the filling yarn is too hard, trouble is met with—it becomes brittle and breaks down the warp yarn.

In my opinion, high pick goods are covered up more than low pick goods. In fact, several things are covered up on high pick goods. On low pick goods little white balls or broken filaments, between the reed and the harness, are sometimes met with. These little balls go right through the weaving and show up in the cloth. The cloth room inspection is very critical, and it is things like these that drive the weaver almost to desperation. Under these conditions, it is a difficult problem to get goods through as "A" quality.

Acetate yarns were quite a bugaboo to all weaving plants. One Pennsylvania plant tried a long time to dress acetate yarns successfully. Some of the materials they used were really prohibitive in price, but they continued to use them.

Quite often a new acetate yarn is put out. Experiments have been made on these and all were found to be more receptive to dressing than the older type of acetate yarn on the market.

As a general rule, acetate goods are put through successfully.

If there is anything anyone would like to ask, I will try to answer to the best of my ability.

Discussion

Ques. You mention that you can stretch your rayon yarns 10% to 14%. Does acetate stretch that much, too?

Ans. We get very little stretch on acetate. For a 70-yard cut we dress 77 yards to measure 70 to 71½ yards of cloth. Tests show that we get from 2% to 2½% stretch.

Ques. What is the nature of the sizing material used on acetate yarns?

Ans. A glue base or a casein base and usually a penetrant. It is almost like making a film on glass.

Ques. What is the percentage taken up by acetate compared with viscose?

Ans. On an acetate yarn we get about 4.65% added weight on about a 10-cut warp.

Ques. About the same as viscose?

Ans. A little more than viscose—4.25% for viscose, 4.65% for acetate.

Ques. Do you get about the same penetration on all acetate yarns?

Ans. On the latter types of acetate yarns we get a greater penetration than on the older type. The older type is coated with a paraffin which is repellent to water. I have tried heating the water to 185° F. to 190° F. for this yarn, but found that the paraffin built up on the rolls. Sometimes we'd have as much as one-quarter inch of paraffin wax on the roll of the slasher.

Ques. If you run the dressing very slowly, does it help in the amount you get?

Ans. I know of a plant in New Jersey where they ran only six yards per minute. They obtained very good results, but found this speed to be impractical.

Ques. How do you measure the temperature on the surface of your dry can?

Ans. I took a thermometer and fastened it on the outside while the machine was in operation. I read it after eight minutes, restarted it and read it after eight minutes again, and thus arrived at an average. I found it varied little. If the steam pressure goes down, the surface temperature goes down.

Ques. How much steam in the can?

Ans. From six to eight pounds steam.

Ques. What percentage softener do you use?

Ans. That's more or less up to the person running it. You can use from practically no softener up to as high as 50%. It varies according to the type of cloth you are running and the results you are after. We try to get the softest piece of goods with the minimum amount of size in it. Of course, once in a while we get variations.

Ques. You mention that you find paraffin wax in one type of acetate yarn. I believe they use an olive oil emulsion on this.

Ans. Well, it looks and smells like paraffin.

Ques. Does a yarn sometimes come with a considerable amount of oil in it?

Ans. At times we have found a yarn which it is practically impossible to dress. About a year ago we had a shipment of viscose process yarn. We put it through in the regular way, but found that the oil in it made it repellent to the size we were using, and when it got to the looms we could not move it. Now, on every production that comes through we take a 2-cut warp and try that out first.

Ques. Does the percentage of size absorbed by the yarn vary with the strength of the solution?

Ans. If you increase the strength of your solution, it does not make much difference—not over 1% at most.

Proceedings of the American Association of Textile Chemists and Colorists

The Use of Monel Metal Equipment for Dyeing with Developed Colors, Stripping and Bleaching

By F. L. LaQUE

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IN choosing a topic for discussion before you gentlemen it occurred to us that a useful guide to your general, technical interest in Monel Metal would be provided by reference to our files as to the questions most commonly asked in letters from the textile industry. As a result it was indicated that some notes on dyeing with developed colors (diazotizing), stripping, and bleaching with both chlorine and peroxide in Monel Metal equipment would prove interesting and, we hope, useful to the industry. While most of the data to be presented will refer to Monel Metal, they will apply as well to nickel which is coming into extensive use in the form of nickel clad steel.

As is well known, the process of dyeing with developed colors consists of (1) the application of the color as ordinarily practised with direct colors, (2) a rinsing operation, (3) treatment in the diazotizing bath, (4) a rinsing operation, (5) a developing operation, (6) rinsing and various finishing operations.

Our interest lies almost entirely in the diazotizing operation for the reason that the chemicals used are very corrosive to metals. The diazotizing bath contains sodium nitrite and sufficient of either sulphuric acid or hydrochloric acid to convert the sodium nitrite into nitrous acid, which becomes the active constituent of the bath, both from the standpoint of the diazo reaction and of the corrosion of metals. Neither hydrochloric acid nor sulphuric acid in the concentrations used is, by itself, active in corroding Monel Metal.

In an experimental study of the corrosion of Monel Metal by diazotizing solutions the following facts were discovered:

1. Corrosion is greater in a diazotizing bath in which no goods are being treated than in one in which the diazo reaction is in progress. In the latter case the greater part of the nitrous acid is rapidly consumed in the reaction.
2. The rate of corrosion varies directly with the *concentration* of the nitrous acid.
3. Pure nitrous acid solutions prepared with hydrochloric acid are more corrosive than those prepared with sulfuric acid, and an excess of hydrochloric acid over the amount theoretically required causes a greater acceleration of corrosion than a similar excess of sulfuric acid.
4. The rate of corrosion at room temperature is twice that at 0°C. (32°F.).
5. All other factors being constant the rate of corrosion is decreased about 20% when the quantity of dyestuff used is increased from 5% to 15% of the weight of the goods.

Considering only the corrosion of metals the practical application of these findings might be as follows:

1. Since it is the nitrous acid in excess of that required for the diazo reaction which is active in corroding metals the quantity of chemicals used should be carefully controlled so as to avoid the formation of an excess of nitrous acid. Also, the quantity of exhausting salt used in the preparation of the dyeing solution will indirectly influence the corrosion of metals in the diazotizing bath as it affects the amount of dyestuff precipitated on the goods, and thereby carried over into the diazotizing bath. It is conceivable, from the corrosion standpoint alone, that a not too careful rinse following the dyeing operation might be beneficial, since it would result in carrying over into the diazotizing bath an excess of dyestuff which would act as a buffer against an excess of nitrous acid.
2. Decreasing the *concentration* of nitrous acid by running as "long" a bath as possible can be expected to cut down the rate of corrosion. This is, of course, limited by the capacity of the dyeing machine, but it would be advisable to keep the volume of the diazotizing bath as large as is consistent with good practice.
3. Sulphuric acid should be used rather than hydrochloric acid in the diazotizing bath.
4. The diazo reaction should be carried out at as low a temperature as is feasible.
5. It is not likely that the quantity of dyestuff used can be manipulated for the sake of avoiding corrosion, but it is conceivable that some relation might be worked out between the percentage of dye-

stuff and the amount of chemicals used in the diazo reaction which would tend to keep the amount of nitrous acid as close as possible to the theoretical amount required by the dyestuff on the fiber, and thus avoid an excess available for corrosion.

6. If a metal dyeing machine is to be used solely and continuously for dyeing with developed colors its life will necessarily be limited. However, where only an occasional lot is dyed with developed colors, no trouble should be experienced, especially where the diazo-reaction is carefully controlled along the lines of the suggestions given above.

Stripping Agents

Monel Metal dyeing equipment has been found to be satisfactory for stripping operations. As a result of improper use of the stripping chemicals the metal may acquire a brown tarnish which can be removed without difficulty, and which can be avoided with equal facility. Obviously, the latter practice is to be preferred. The following notes on the use of some common stripping agents may be helpful in this respect:

1. *Sodium Hydrosulphite* $Na_2S_2O_4$
   (Also called Hydrosulphite, Lykopon, Blankit, etc.)
   In using sodium hydrosulphite as a stripping agent it is necessary to maintain the bath at a calculated pH of 10.8 or higher, in order to prevent rapid decomposition of the chemical. Such practice will, at the same time, insure against discoloration of Monel Metal exposed to the stripping bath. It is common to attain the desired alkalinity by the use of ammonia. However, due to the high volatility of ammonia it may sometimes happen that sufficient will be lost by evaporation during the stripping process to allow the pH to fall below the critical value, with consequent staining of the metal. To avoid this, an excess of ammonia may be added at the start, or additions of ammonia may be made during the process to make up for the evaporation losses. Another alternative is to use soda ash as the source of the alkalinity, bearing in mind, of course, that it should be used with care so as to avoid harshening of the goods. Soda ash has the virtue that, since it is not volatile, the alkalinity of the bath is maintained throughout the operation.
2. *Basic Zinc Sulphoxylate Formaldehyde-Zn*$(OH)HSO_2CH_2O$
   (Also called Formapon X, Decroline, etc.)
   This compound is used for stripping in an acid solution. It has been found that no discoloration of Monel Metal will occur if the pH of the solution is kept higher than 3.2. Comparatively large excesses of acetic acid may be used without lowering the pH below this critical value. However, the pH will be lowered and discoloration will occur if an excess of a stronger acid, such as formic acid or sulphuric acid, be used. The use of acetic acid is, therefore, suggested for stripping with this compound in Monel Metal machines since less care will be required in controlling the amount of acid used. A leading manufacturer recommends that the acid and the stripping agent be mixed cold in a pail or barrel just before adding to the boiling bath.
3. *Normal Zinc Sulphoxylate Formaldehyde-Zn*$(HSO_2CH_2O)_2$
   (Also called Protolin, Soluble Decroline, etc.)
   This compound is similar to the basic Sulphoxylate formaldehyde already discussed and the same comments apply to its use in Money Metal equipment.
4. *Sodium Sulphoxylate Formaldehyde-*$NaHSO_2CH_2O\ 2H_2O$
   (Also called Formopon, Rongalite, etc.)
   This compound finds its principal application in printing cotton and is seldom used for stripping. Because of its high alkalinity, the compound is too slow in its action to be serviceable as a stripping agent and, if acid is added, it breaks down so rapidly that difficulties are encountered and Monel Metal becomes discolored. Therefore, its use with acids in Monel Metal machines should be avoided. When used in contact with Monel Metal without the addition of an acid it is sometimes desirable to add about 2% of ammonia (28%) or 1% of soda ash on the weight of the goods.
5. *Stabilized Titanium Sulphate*
   Titanium compounds are used occasionally as stripping agents. A manufacturer has reported that these compounds have been tested in their laboratory and have no effect on Monel Metal. They recommend that the goods be kept constantly in motion during the stripping process.

If, for any reason, Monel Metal should become discolored by a stripping agent, the discoloration can readily be removed by the use of a hot, or boiling, solution containing from 0.25% to 1% of potassium cyanide, as suggested by H. Kay in "The Dyer and Calico Printer" November 1929, page 471. In view of the poisonous nature of this chemical extreme precautions will be necessary in using this method of removing the discoloration. An alternative method is the use of a boiling, dilute solution of sulfuric acid made oxidizing by the addition of hydrogen peroxide. The amount of each chemical required for any specific case is best determined by trial.

Data on the properties and use of stripping agents are contained in the following papers:

1. Stripping Hosiery with Hydrosulphites and Sulphoxalates. A. R. Thompson American Dyestuff Reporter, June 2, 1924.
2. The Manufacture and Use of Hydrosulphites. C. S. Hollander, American Dyestuff Reporter, November 1, 1926.

Bleaching With Chlorine

As is well known, solutions containing appreciable concentrations of available chlorine are very corrosive to metals; even gold is not immune to attack. In fact, one of the earliest processes for the extraction of gold from its ores consisted of a treatment of the finely divided ore with solutions containing chlorine as their active ingredient. It is not surprising then, that it is advisable to be careful in the use of metal dyeing equipment for chlorine bleaching. Under the conditions of service to be described below, Monel Metal equipment has been found to be very satisfactory both in the dyehouse and in the laundry.

Calcium Hypochlorite Solutions

Degrees Twaddle	Specific Gravity	Available Chlorine g. p. l.	Available Chlorine oz. p. gal.	Chloride of Lime oz. per gal.*
1/8	1.0006	0.35	0.0465	0.16
1/4	1.0011	0.70	0.0931	0.32
1/2	1.0025	1.40	0.1862	0.64
3/4	1.0037	2.05	0.2727	0.94
1	1.0050	2.71	0.3604	1.24
1 1/4	1.0062	3.38	0.3495	1.55
2	1.010	5.38	0.7421	2.57
5	1.025	14.47	1.9245	6.64
10	1.050	29.41	3.9115	13.50
20	1.100	61.17	8.1356	28.08

*Quantity of Bleaching Powder added to each gallon of water in making up the solution.

The horizontal line marks the limiting concentration of available chlorine for successful use of Monel Metal equipment.

Monel Metal should not be used in contact with solutions containing more than 3 grams per litre of available chlorine. This is not a serious limitation since solutions containing more than this concentration of chlorine are not in common use for textile bleaching in equipment apt to be constructed of Monel Metal.

For convenient reference the accompanying tables show the relation between the specific gravity of various hypochlorite solutions and their available chlorine content.

Also it should be remembered that Monel Metal is not recommended for use in *continuous* contact with bleaching solutions even where the concentration of available chlorine is below the prescribed limit of 3 grams per litre. In practice this amounts to saying that Monel Metal equipment is satisfactory where the bleaching, rinsing and souring operations are carried out in cyclic order in the same machine, but that Monel Metal should not be used as a container for chlorine solutions in processes *where the goods are moved* from one machine to another for each of the operations and where, therefore, the chlorine solution in the Monel Metal tank would be kept up to strength by periodic additions of a strong chlorine solution. Such processes are commonly used for the bleaching of lace and rayon where the goods are wound on reels which are moved automatically through the bleach baths, sours and final rinses in cyclic order. While Monel Metal should not be used for holding the bleaching solution in connection with these processes, it is suitable for reels, and other material carrying devices, which are in

Sodium Hypochlorite Solutions

Degrees Twadell	Sodium Hypochlorite made with caustic soda: Specific Gravity	Available g. p. l.	Chlorine oz. p. gal.	Sodium Hypochlorite made with caustic soda and soda ash*: Specific Gravity	Available g. p. l.	Chlorine oz. p. gal.	Sodium Hypochlorite made with soda ash: Specific Gravity	Available g. p. l.	Chlorine oz. p. gal.
1/4	1.001	0.60	0.0798	1.001	0.40	0.0532	1.001	0.37	0.0492
1/2	1.002	1.20	0.1596	1.002	0.80	0.1064	1.002	0.74	0.0984
3/4	1.003	1.90	0.2527	1.003	1.20	0.1596	1.003	1.10	0.1463
1	1.005	2.50	0.3325	1.005	1.80	0.2394	1.005	1.50	0.1994
1 1/4	1.006	3.10	0.4123	1.006	2.15	0.2859	1.006	1.90	0.2527
1 1/2	1.007	3.70	0.4921	1.007	2.35	0.3025	1.007	2.20	0.2926
1 3/4	1.008	4.30	0.5719	1.008	2.80	0.3724	1.008	2.70	0.3591
2	1.010	4.90	0.6517	1.010	3.40	0.4522	1.010	3.00	0.3990
5	1.025	14.47	1.9251	1.025	8.35	1.1105	1.025	7.0	0.9310
10	1.050	28.5	3.79	1.050	16.7	2.221	1.050	14.0	1.862
20	1.100	57.0	7.581	1.100	33.4	4.442	1.100	28.0	3.724
30	1.150	84.0	11.172	1.150	50.0	6.650	1.150	42.0	5.586

*These values apply to a mixture of twenty parts soda ash to eight parts caustic soda which is a typical ratio for a solution of the mixed type.

The horizontal lines mark the limiting concentrations of available chlorine for the successful use of Monel Metal equipment.

contact with the bleach bath for a relatively short period and pass through the souring and rinsing solutions as well.

Monel Metal should not be used for containers for the manufacture or transportation of stock chlorine bleaching solutions nor should Monel Metal pails or dippers be used for carrying such stock bleach solutions around the dyehouse. In making up the bleaching bath it is desirable to dilute the stock bleach well before adding it to the machine or dye kettle and to add it to as large a volume of water as possible.

Experiments have shown that sodium silicate (water glass) when added to hypochlorite solutions acts as a powerful inhibitor of corrosion; concentrations of sodium silicate as low as 0.5 gram per litre have been found to be effective. In special cases this property of sodium silicate may be found to be useful.

This discussion of the behavior of Monel Metal in contact with chlorine bleaching solutions should enable the user of Monel Metal equipment to use it with assurance for the bleaching of goods by the method outlined, that is, using solutions containing less than 3 grams per litre of available chlorine and following the bleach bath by rinses and sours in the same machine or dye kettle, and to avoid any difficulties which might attend the improper application of the metal.

Bleaching with Hydrogen Peroxide

Monel Metal equipment has been found to be very satisfactory for bleaching wool, silk and cotton in alkaline solutions containing hydrogen peroxide. The following quotation from a letter received from a leading manufacturer of hydrogen peroxide may be of interest in this connection:

"We have subjected the Monel Metal and nickel containers you forwarded to us for experimental purposes to a long series of tests in conjunction with bleaching textiles and we find both metals extremely satisfactory for use in connection with Hydrogen Peroxide bleaching. Both the experimental bleaching vessels have stood up wonderfully throughout the tests and an excellent factor as to their suitability for bleaching is their non-oxidizing properties. The bleaching vessels were at all times clean and we find that their action as a catalyst in connection with a Hydrogen Peroxide bleaching solution is almost nil."

No special care is required in the use of Monel Metal equipment in contact with peroxide bleaching solutions prepared either from sodium peroxide or by the use of hydrogen peroxide as such. However, certain precautions are necessary in the *preparation* of a bleaching solution using sodium peroxide and sulphuric acid.

The common method of using sodium peroxide is to add it to a bath containing the required amount of sulphuric acid and then to add ammonia or sodium silicate to adjust the alkalinity of the solution to the proper value. If this process were to be carried out in a Monel Metal kettle or machine, a small quantity of metal would be taken into solution by the strongly oxidizing acid solution resulting from the addition of sodium peroxide to the acid bath. While the amount of metal dissolved would not be large enough to shorten the life of the equipment appreciably the bath would suffer some loss of bleaching power and when the addition of alkali was made the dissolved metal might be precipitated in the form of insoluble compounds which would get into the goods.

These difficulties can be avoided in either of two ways:

1. Since Monel Metal is free from attack by peroxide solutions so long as they are neutral or alkaline, the bleach bath can be made up by first dissolving the sodium peroxide in water in the Monel Metal equipment, then adding the required acid to the point of neutrality followed by the addition of ammonia or sodium silicate to the desired alkalinity. With this method an oxidizing acid solution will never be formed and, therefore, no corrosion of the metal or decomposition of the solution will occur.
2. The sodium peroxide and acid can be mixed in the usual way in a crock or wooden tub outside the Monel Metal machine or kettle and then added to an alkaline solution in the Monel Metal equipment.

The latter method is usually preferred since the solution of sodium peroxide in water is rather slow. However, it has been found that satisfactory bleaching can be accomplished in Monel Metal equipment by either method.

Most of the following list of papers on peroxide bleaching contain references to the use of Monel Metal equipment for peroxide bleaching:

1. Hydrogen Peroxide Bleaching
   I. E. Weber
   Textiles, December, 1923, page 61.
2. Bleaching with Peroxides
   T. D. Ainstee
   American Dyestuff Reporter, Sample Swatch Quarterly, March 22, 1926, page 203.
3. Bleaching Wool With Hydrogen Peroxide
   H. G. Smolens
   American Dyestuff Reporter, February 6, 1928, p. 79
4. Bleaching Silk-Cotton Hosiery with Hydrogen Peroxide
   H. G. Smolens
   American Dyestuff Reporter, May 14, 1928, page 309.
5. Peroxides for Textile Bleaching
   H. G. Smolens
   American Dyestuff Reporter, Sample Swatch Quarterly, October 15, 1928, page 672
6. Hydrogen Peroxide Bleaching of Wool, Silk and Cotton Under Chemical Control
   H. G. Smolens

American Dyestuff Reporter, Feb. 18, 1929, page 123

7. Effect of Copper and Lead Ions upon the Rate of Decomposition of Hydrogen Peroxide at Various Acidities
H. W. Rudel and M. M. Haring
Industrial & Engineering Chemistry, Vol. 22, No. 11, November, 1930, page 1234
8. Peroxide Bleaching of Silks
T. D. Ainstie and L. P. Litchfield
The American Silk Journal, December, 1931.

ACKNOWLEDGMENT

The author is grateful to the Röhm and Haas Company, Philadelphia, Pennsylvania, for data on stripping agents and to the Buffalo Electrochemical Company, Buffalo, New York, and the Roessler and Hasslacher Chemical Company, Perth Amboy, New Jersey, for data on peroxide bleaching. Most of the data on diazotizing and chlorine bleaching were obtained by Messrs. O. B. J. Fraser and H. E. Searle of the Development & Research Department, The International Nickel Company, Inc., New York; Dr. W. A. Wesley of the Research Laboratory, International Nickel Company, Bayonne, New Jersey, contributed much of the data on stripping agents vs. Monel Metal. The help of these colleagues is gratefully acknowledged by the author.

DISCUSSION

Ques.: I'd like to ask about the rinsing. Why do you get better results with incomplete rinsing? Is it the color that acts with the nitrous acid in preference to the metal?

Mr. LaQue: The idea is to be sure that there is enough dyestuff carried over into the diazotizing bath to use up all the acid. I have not been able to find out definitely whether the amounts of sodium nitrite and acid used are determined by the weight of the goods or by the amount of dyestuff used.

Answer from floor: The goods.

Mr. LaQue: Is that necessary or could they be more closely related to the weight of the dyestuff?

From floor: They could be adjusted for the depth of shade you are dyeing, but we have been told that the amount should be figured on the weight of the goods. It seems that some dyers go to extremes and use amounts of nitrite and acid far beyond those required.

Mr. LaQue: It has been my impression that in many cases an unnecessarily large excess of nitrous acid is formed.

Ques.: In your discussion of diazotizing, you rather avoided the dyer's end of it and stuck to a discussion of the reactions on the metal. The important thing is to determine whether you can diazotize. Is there any effect on the shade? I should like to ask whether the suggestions you made towards eliminating corrosion would prove equally as useful in minimizing any effects on shade.

Ans.: It has never been reported to us that corrosion of metal dyeing equipment by the diazotizing solution was accompanied by any difficulty in obtaining the proper shade even in those cases where apparently careless control of the diazotizing chemicals resulted in appreciable corrosion of the metal. It was mainly from the standpoint of increasing the life of the equipment that careful control of the diazotizing chemicals was suggested.

Ques.: In regard to stripping with alkaline hydrosulphite, did you find one that worked well?

Ans.: A solution of sodium hydrosulphite adjusted to a pH higher than 10.8 will strip satisfactorily and will not discolor the metal.

Ques.: You are speaking of stripping cotton?

Ans.: So far as I know the nature of the fiber is not important except as it may effect a change in the pH of the stripping bath which should be controlled as suggested.

Ques.: Have you had much complaint as to the effect of the metal on the shades of pastel shades on wool?

Ans.: We have had a few complaints on that score. Evidently there are a few dyestuffs, confined mostly to chrome mordant colors, which are affected by Monel Metal, due probably to the effect of the dichromate which acts as an oxidizing agent and increases the rate of corrosion of the metal by the acid. However, the number of dyestuffs so affected is limited to a relatively few colors. For example, a prominent European manufacturer of dyestuffs recently determined the effect of Monel Metal on some 193 chrome acid colors on wool and found that only six colors were noticeably affected and only one color seriously affected. We were fortunate in obtaining samples from these test dyeings which have been mounted in a book which I have with me and which you are free to examine after the meeting. We have found that where the metal has a slight effect on the shade this effect can be greatly reduced by the use of ½% of ammonium sulphocyanide on the weight of the goods. You may be interested to learn that we are at the present time experimenting with a new alloy of nickel and chromium which was developed primarily for the handling of foodstuffs but which gives promise of being very useful for wool dyeing since such tests as have been made indicate that it has practically no effect on even the most sensitive dyestuffs.

Ques.: Is it the copper contained in Monel Metal which is responsible for such effects on shade as are noticed?

Ans.: It is well known that Monel Metal has considerably less effect on shades than pure copper. This suggests that nickel is relatively inert in such respects. While we have found that nickel is usually somewhat superior to Monel Metal in its effect on the few shades

that are changed it is probable that very sensitive dyestuffs would be affected somewhat by nickel as would be the case with any of the heavy metals taken into solution.

Ques.: Why should ammonium acetate give more color change than acetic acid?

Ans.: If the color change is assumed to be entirely due to dissolved metal it would be reasonable to suppose that the ammonium acetate solution dissolved more metal than the acetic acid.

Ques.: How about sulphur colors?

Ans.: If equipment is to be used entirely for sulphur colors we ordinarily do not suggest Monel Metal since plain iron or steel would be adequate. However, where many types of color are to be used Monel Metal is recommended since it lends itself well to all. Monel Metal equipment is being used extensively for the dyeing of sulphur colors.

Ques.: What do you recommend for cleaning the metal?

Ans.: If sulphides are to be removed we have found that the quickest solvent for nickel and copper sulphides is sodium or potassium cyanide. That does not necessarily mean that the cyanide method is the best since the poisonous nature of the compound introduces obvious difficulties in its utilization. We often suggest the use of an oxidizing acid solution such as boiling dilute sulphuric acid plus a small quantity of hydrogen peroxide which we have found to be effective.

Ques.: Are there any chemicals which crystallize Monel Metal and make it brittle?

Ans.: The supposition that metals become brittle due to recrystallization as a result of vibration or chemical action, etc. has been shown to be erroneous and is no longer given serious consideration. Many metals when in a state of strain are subject to cracking as a result of contact with solutions containing salts of mercury. There have been a few cases where Monel Metal has suffered such embrittlement but they have been rare and confined to specific conditions which can and should be avoided.

Ques.: Does amalgamation occur?

Ans.: Yes, in the presence of an electrolyte and under suitable conditions the fracture of metal embrittled by mercury will show some amalgamation.

Ques.: What do you recommend for bleaching out a kettle that has some wooden parts—chrome vitriol or bleaching compound?

Ans.: The chrome vitriol appeals to me as being less corrosive. While it is somewhat corrosive to Monel Metal the rate of attack is not alarmingly high and since the time of contact would be limited no serious corrosion would result.

Ques.: What do you recommend for removing ordinary scum from dyeing equipment?

Ans.: It depends on the nature of the scum, but we ordinarily recommend a soda ash boil.

From the floor: At one time we had some trouble in cleaning up a kettle used for soap scouring and acid dyeing. The metal acquired a deposit of a thick, black, gummy substance which was difficult to remove. We finally wiped it off with a mixture of pine oil and sulphonated castor oil.

Mr. LaQue: I am glad to learn this method of removing scum.

From the floor: The mixture of pine oil and sulphonated castor oil removes the scum very easily when applied with a cloth. To avoid formation of such scums we use the same materials as additions to the scouring bath.

Ques.: Is there any metal that will stand acid peroxide?

Ans.: I suggest that you investigate alloys containing appreciable percentages of chromium. If the acid involved is not ordinarily corrosive to Monel Metal or nickel, these metals should be tried since they would probably be useful.

Ques.: When a crack starts in a tank lining how do you stop it?

Ans.: The best method is to cut out a piece containing the cracked area and put in a patch. It is well to cut beyond the visible limits of the crack, since a very fine crack may extend farther than one can see with the naked eye. If the cracking is bad and is due to some inherent defect in the tank lining such as a poor fit or excessive buckling the best thing is to put in a new lining using a heavy enough gauge of metal to make a strong good fitting lining.

Ques.: Is there any way to prevent pitting?

Ans.: Pitting of metals is usually less a function of the metal than of the solution responsible for the pitting. It can often be traced to films normally present on the metal or formed by corrosion. Some films are protective and others are just the reverse. In both cases the effect of discontinuous films is to localize corrosion in the form of pits. As an example, the films formed on many metals by acetic acid often result in pitting. In this respect acetic acid is much worse than sulphuric acid.

Ques.: How about formic acid?

Ans.: Formic acid behaves more like acetic acid than like sulphuric acid.

Ques.: Is phosphoric acid corrosive?

Ans.: Chemically pure phosphoric acid is not especially corrosive; however, when it contains oxidizing impurities such as ferric iron salts it becomes quite corrosive to many metals and alloys. For this reason it is difficult to make a general statement as to the corrosiveness of phosphoric acid.

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Devoted to the use and application of dyestuffs and the mechanical equipment incidental thereto.

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SPREADING WORK

HOW firms in the textile industry have maintained employment through shorter working hours and division of work among their employes is told in a report prepared for the President's Organization on Unemployment Relief and being distributed to industrial firms in all sections of the country.

Shorter hours per day or week, staggering of shifts, shorter shifts in continuous operation, rotation of days off, and similar expedients have proven successful in many industries, the report shows. Numerous examples are cited to show the latest practice as progressively developed during the present emergency with a view to providing work for as many employes as possible.

Wide-spread progress toward shorter hours in the cotton industry has been accomplished under the auspices of the Cotton Textile Institute. The elimination of night work for women and minors, reduction of day time operation to 55 hours per week, and, where night shifts are operated, to 50 hours, and the discontinuance of over time during the noon luncheon period have been adopted by a preponderant part of the industry.

The long-time effect sought is to help prevent recurrent periods of over production and under employment. Results already are evident according to a recent statement by George A. Sloan, President of the Institute.

Numerous firms in all branches of the textile industry and related lines have adopted emergency plans to retain their working forces by dividing available employment.

The Crompton & Knowles Loom Works, Worcester, Massachusetts, has followed a policy of developing new products to give employment. In December, this firm was keeping at least 10 per cent of its force on development work, who would otherwise have been jobless. New products have been responsible for keeping at least 25 per cent of the present force employed during 1930 and 1931.

The Textile Machine Works, Reading, Pennsylvania, is carrying out an enlarged program of overhauling and repairing equipment and buildings and has undertaken the construction of residential buildings.

This policy of dividing the available amount of labor and increasing work on improvement projects is certainly to be commended and should receive the endorsement of many other firms.

IMPROVING THE STATUS OF RAW SILK

A CONSTRUCTIVE step was taken at the Knitting Arts Exhibition, held last week in Philadelphia, when a conference was held for the purpose of deciding on a program that would improve the status of raw silk. The outstanding occurrence at this session was the address delivered by D. E. Douty, in which he analyzed the problems of "two tone effect" and gave valuable suggestions calculated to be of specific help to this branch of the industry. Mr. Douty said, in this respect:

"The situation is difficult, perhaps discouraging, but it is not hopeless. The first and most important thing to do is to take steps to impress upon the primary market that a bale or group of bales constituting a lot shall be uniform in nature, color, type, district, and season of cocoons, size, etc., even if it is necessary to group bales in less than ten bale lots.

"The new conditions which are introduced in the Yokohama and Kobe markets January 6, 1932, are both favorable and unfavorable to securing desirable results. Since that date, all raw silk intended for export must be bought and sold on the certificate of grade issue either the Yokohama or Kobe Imperial Conditioning House and the certification of grades by either is final. No silk is allowed to be shipped unless it has been inspected, tested, certificated and sealed by the Testing House and it must leave the port with seal unbroken.

"If the conditions, which are causing trouble in the knitters' raw silk supply can be remedied, either in the production, merchandising, or packing of raw silk in Japan, the Imperial Government certainly has the power and facilities to correct them.

"Through your association (the National Association of Hosiery and Underwear Manufacturers) you have a powerful means for collective and co-operative action . . . It is, therefore, incumbent upon the associations to make a thorough study of the conditions of raw silk supply, become accurately informed upon its ramification and to take active part in the co-operation with the Silk Association of America in every way to safeguard your supply and to facilitate your raw silk transactions."

German Chemical Industry Seen as Over-expanded

The development of self-sufficient chemical industries in countries which were formerly dependable outlets for German chemical products is an outstanding factor in the decline of the German chemical industry during the last two years, according to Consul General W. L. Lowrie, Frankfort-on-Main, in a bulletin just issued by the Commerce Department. Intensified competition by the other large chemical-producing countries has also been severely felt by German producers, he points out.

The possibility of these developments, according to the consul-general's report, was overlooked or ignored while the German industry was expanding and rationalizing after the war on a gigantic scale, calculated in many instances to supply the world. German production capacity for nitrogen and potash is at present sufficient to supply all countries, while the output of dyestuffs and pharmaceuticals is also adjusted to supply the largest part of the world requirements. That Germany's chemical industry has been overbuilt is now realized by German industrialists and economists, the report states.

Reviewing developments in the German chemical industry in 1931, the report shows that estimated production showed a decline of about 11 per cent; unemployment rose from 21.6 per cent in December, 1930 to 27.1 per cent in October, 1931. Wholesale prices in general were downward, although prices of numerous chemical products were well maintained. Production of dyes, pharmaceuticals, and photographic chemicals held up rather well during the year.

German foreign trade in chemicals and allied products declined in line with that of other countries. Exports which amounted to a total of $254,000,000 registered a drop of 15 per cent. Gains, however, were recorded in some branches, especially in prepared medicines and to a lesser degree in industrial chemicals and coal-tar dyes. Total imports of chemicals and allied products registered a decline of 26 per cent, having a value of $73,100,000.

Very little was done in the promotion of cartels and combines in 1931, although absorptions and mergers of German concerns continued. Of outstanding importance was the termination of the International nitrogen agreement in the summer of that year. Germany has also lost ground in its export markets for potash, a commodity in which it formerly had a world monopoly, since now several European countries, as well as the United States, are able to furnish at least a part of their own requirements.

NEW PATENTS

(*Abstracted by Synthetic Organic Chemical Mfrs. Assn.*)

Process of Preparing 2:4-Di-Nitrophenyl-6-Hydroxytriazine-1:3:5. (Dyestuffs and pharmaceutical intermediate, comprises treating 2:4-diphenyl-6-hydroxytriazine-1:3:5 with a nitrating agent.) Winfrid Hentrich, of Wiesdorf-on-the-Rhine, and Josef Hilger, of Cologne-Mulheim, Ger., assignors to General Aniline Wks., Inc., of N. Y., N. Y., No. 1,841,440, January 19, 1932.

4'-Methyl-6-Halogen Thioindigos and Their 6'-Halogen Derivatives. (Dye cotton from yellow vats bluish pink to red shades.) Richard Herz, of Frankfort-on-the-Main, and Walter Brunner, of Frankfort-on-the-Main-Fechenheim, Ger., assignors to General Aniline Wks., Inc., of N. Y., N. Y., No. 1,841,441, January 19, 1932.

Mordant Dyestuffs of the Thiazine Series. (Particularly mordant dyestuffs obtainable by treating hydroxysulfoaryliminonaphthoquinones with sulfurizing agents; dye wool from an acid bath reddish violet shades becoming greenish when after-chromed; also for printing wool or cotton according to the chrome-printing processes.) Richard Herz and Norbert Steiger, of Frankfort-on-the-Main, Ger., assignors to General Aniline Wks., Inc., of N. Y., N. Y., No. 1,841,442, January 19, 1932.

Manufacture of Pyrazolone Compounds. (Dyestuff intermediates, for instance, diphenyl sulfides which may be converted into azo dyestuffs by coupling them with diazo compounds; show excellent fastness to washing and suitable both as acid colors for animal fibers and chrome printing colors for cotton; shades vary from greenish-yellow to reddish-orange.) Mordecai Mendoza, of Blackley, Manchester, England, assignor to British Dyestuffs Corp., Ltd., of Manchester, England, No. 1,841,621, January 19, 1932.

Intermediates and Dyes Therefrom. (An extension of various other patents.) Mordecai Mendoza, of Blackley, Manchester, England, assignor to British Dyestuffs Corp., Ltd., of Manchester, England, No. 1,841,622, January 19, 1932.

New Pyrazolones and Dyes Therefrom. (An extension of above patents.) Mordecai Mendoza, of Blackley, Manchester, England, assignor to Imperial Chemical Industries Ltd., of London, England, No. 1,841,623, January 19, 1932.

Azo Dyestuffs. (A division of above patent No. 1,841,636.) Kenneth Herbert Saunders and Mordecai Mendoza, of Manchester, England, assignors to British Dyestuffs Corp., Ltd., of Manchester, England, No. 1,841,637, January 19, 1932.

Process of Preparing Ortho'-Ortho'-Dicarboxyl-Diphenyl-Diamino Anthraquinone. (Dyestuff intermediates, an improved process which comprises heating a dihalogen anthraquinone body with an antranilic acid body in a low boiling alcohol under pressure in the presence of a copper catalyst.) William L. Rintelman, of Milwaukee, and Robert J. Goodrich, of So. Milwaukee, Wis., assignors, by mesne assignments, to E. I. duPont deNemours & Co., No. 1,841,674, January 19, 1932.

Emulsive Capacity of Sulphonated Oils*

Miscibility of Sulphonated Oils and Neutral Oils

By **RALPH HART**

The Hart Products Corp., 1440 Broadway, New York, N. Y.

The Emulsive Capacity of a sulphonated oil is determined by mixing it with various amounts of olive oil, clearing with oleic acid, and finally testing the stability of the emulsion. The emulsive capacity is useful in formulating commercial products, and serves also as a criterion of quality and as a means of idenification.

Judging by the amount of oleic acid required to produce uniform mixtures, sulphonated oils are more miscible with mineral than with fatty oils, and both fatty and mineral oils are less miscible with sulphonated castor than with sulphonated olive oil. Sulphonated oils are better emulsifiers for mineral than for fatty oils; in this respect, acid sulphonated castor oil is inferior to acid sulphonated olive oil. Complete neutralization of a sulphonated oil decreases its miscibility with neutral oils. Completely neutralized sulphonated oil, with the proper addition of alcohol, is a better emulsifier for mineral oils than the acid oil but is a poorer emulsifier for fatty oils.

SULPHONATED oils find varied and extensive application in the industries, being used as mordants, dye assistants, detergents, softeners, wetting - out agents, etc. They are particularly useful to the manufacturer of specialty oils for making soluble or emulsifying immiscible liquids, such as fatty oils, mineral oils, and solvents. Many bleach or kier oils on the market are mixtures of sulphonated oil and pine oil or another solvent; wool, silk, and rayon oils are often mixtures of sulphonated oil and mineral, neatsfoot, olive oil, or a similar lubricant. Sulphonated oil also forms the base in the so-called soluble cutting oils for metals, and finally sulphonated cod or other fish oil is used considerably in treating leather.

The emulsifying property of sulphonated oils depends to a great extent upon the nature of the raw oil, method of sulphonation, neutralization of the finished product, moisture content, etc. Geronazzo[2], in discussing leather oils, states that the quality of a sulphonated oil is related directly to the duration of its own emulsion and to its "emulsive capacity"—i.e., the property of retaining a definite quantity of another fatty substance in a homogeneous emulsion. Bumcke[1] concludes that sulphonated oils with the greatest carrying capacity for mineral oils give the best results in practice. In spite of its evident importance there seems to be no detailed procedure in the literature for determining the meulsifying capacity of sulphonated oils; hence the simple method outlined in this paper may be timely. This test is of importance not only in formulating commercial products, but is useful also as a criterion of the quality of the oil and as a means of identification.

A sulphonated-oil mixture to be marketable must be uniform and clear and remain so indefinitely. It has also been found that a clear oil gives a better emulsion than a cloudy product, which may separate on standing. Homogeneity is usually attained by adding oleic acid (red oil) to the mixture[3]. An excess of oleic acid, however, must be avoided as it may exert a de-emulsifying effect upon the mixture.

Procedure

To determine the emulsive capacity, the writer proposes to find the maximum amount of olive oil which, when mixed with 100 grams of the sulphonated oil under examination, gives an emulsion of a definite stability. A mixture of the two oils is usually cloudy but becomes clear upon adding oleic acid. The test consists of two parts: preliminarly emulsions, in which the sulphonated oil varies by 10 per cent intervals; and final emulsions, in which the sulphonated oil varies by 1 or 2 per cent of the mixtures.

Preliminary Emulsions. Ten grams of a mixture of the sulphonated oil and olive oil (9 grams and 1 gram, respectively; 8 grams and 2 grams, respectively, etc.), are thoroughly mixed in a 100-cc. glass beaker, using preferably a thermometer as a stirring rod, and titrated at 40° C. with oleic acid until the mixture just turns clear. Next 0.1 cc. of excess oleic acid is added, and a 5 per cent emulsion made, of which 100 cc. are allowed to stand for exactly 2 hours in a 4-ounce oil bottle. The titration with oleic acid is very sharp and sensitive to less than 0.25 per cent of the mixture. A large excess of oleic acid, for reasons already mentioned, must be avoided. After the 2 hours, the emulsions are closely examined and note made of those showing free oil on the surface. With the preliminary emulsions there is no difficulty in separating the good emulsions from the poor ones, as the change is very marked.

Final Emulsions. Another series of mixtures is now made beginning with the first satisfactory emulsion containing the least amount of sulphonated oil, but instead of 10 grams, a quantity ten times as much is used, or 100 grams. Six mixtures are made, each consecutive one containing 2 grams less of the sulphonated oil. In each case after clearing, 0.5 gram excess of oleic acid is added. Emulsions are made as above, and the first emulsion next to the last one showing free oil is taken as the end point. Of course, the change in the nature of the emulsions is

*Ind. & Eng. Chem.

not so pronounced as in the previous emulsions, but nevertheless is quite distinct, and a 4-gram interval of the sulphonated oil at the crucial point makes the change unmistakable. Table I gives the results obtained in testing a sulphonated olive oil which had an emulsive capacity of 108. The olive oil used with the ordinary denatured oil containing 4.2 per cent free fatty acids; the oleic acid was a straw-colored commercial red oil of low chilling point.

TABLE I. STABILITY OF EMULSIONS OF MIXTURES OF SULPHONATED OLIVE OIL AND RAW OLIVE OIL

Mixture	Sulphonated Olive Oil *Grams*	Raw Olive Oil *Grams*	Oleic Acid To Clear *Cc.*	Stability of Emulsion
		Preliminary Tests		
1	10	0	0.0	Good
2	9	1	0.0	Good
3	8	2	0.0	Good
4	7	3	0.6	Good
5	6	4	1.1	Good
6	5	5	1.6	Good
7	4	6	2.0	Very poor
8	3	7	2.6	Very poor
9	2	8	3.4	Very poor
10	1	9	...	.....
		Final Tests		
11	50	50	16.5	Good
12a	48	52	17.1	Good
13	46	54	17.8	Poor
14	44	56	18.6	Poor
15	42	58	19.8	Very poor
16	40	60	20.8	Very poor

a End point: emulsive capacity = 52/48 × 100 = 108.

RESULTS WITH VARIOUS OILS

The emulsive capacity of some commercial oils employed for different purposes and determined as above are shown in Table II. Samples with low numbers proved, upon further testing, to be either products of poor quality or compounded oils to which a certain amount of fatty or mineral oil had already been added.

TABLE II. EMULSIVE CAPACITY OF SOME COMMERCIAL OILS

Sample	Manufacturer's Description	Emulsive Capacity *Grams*/100 *grams sample*
1 N	Sulph. olive oil	108
2 R	Sulph. olive oil	100
3 L	Sulph. olive oil	85
4 P	Sulph. olive oil	56
5 D	Sulph. castor oil	61
6 P	Sulph. castor oil	61
7 A	Sulph. neatsfoot oil	42
8 L	Sulph. neatsfoot oil	38
9 D	Silk oil	35
10 H	Silk oil	35
11 E	Silk oil	45
12 N	Silk oil	10
13 F	Rayon oil	45
14 N	Leather oil	150

Repeated tests have shown, contrary to the prevailing notion, that mineral oil is more readily emulsified by sulphonated oils than fatty oils, provided the mixture is first made into a clear, uniform oil. Mineral oil is also the more miscible, as shown by the much smaller quantity of oleic acid necessary to clear. This is shown in Table III, in which mixtures of a concentrated sulphonated olive oil (moisture content, 24.3 per cent; free fatty acids, 19.0 per cent; soap, 6.0 per cent) and a light spindle oil (specific gravity, 0.845; viscosity, 80 sec. Saybolt at 37.8° C.) were cleared with red oil.

Judging by the amount of oleic acid necessary to clear a given mixture, sulphonated castor oil is less miscible with mineral or fatty oils than sulphonated olive, or similar oil. In Table IV is listed a series of mixtures of the two sulphonated oils with olive oil, from which will be observed the much greater quantity of oleic acid required to clear mixtures made with the sulphonated castor oil. Where the olive is replaced by mineral oil, the difference is even more market, since a good grade of concentrated sulphonated olive oil will mix with mineral oil practically in all proportions without any addition of oleic acid, whereas it is always required in the case of sulphonated castor oil, often to the extent of 25 per cent of the mixture. The difference is still further intensified by completely neutralizing the sulphonated oils. The sulphonated castor oil used in Table IV was of good quality, containing about 25 per cent moisture.

TABLE III. OLEIC ACID REQUIRED TO CLEAR MIXTURES

(Sulphonated olive oil and mineral oil; sulphonated olive oil and olive oil)

Mixture	Sulphonated Olive Oil *Parts by wt.*	Mineral or Olive Oil *Parts by wt.*	Emulsions: Mineral oil mixtures	Emulsions: Olive oil mixtures	Oleic Acid to Clear: Mineral oil mixtures % *in cc.*	Oleic Acid to Clear: Olive oil mixtures % *in cc.*
1	100	0	Good	Good	0	0
2	90	10	Good	Good	0	0
3	80	20	Good	Good	0	0
4	70	30	Good	Good	0	6
5	60	40	Good	Good	0	11
6	50	50	Good	Good	0	16
7	40	60	Good	Very poor	2	20
8	30	70	Fair	Very poor	5	26
9	20	80	Poor	Very poor	6	34
10	10	90	None	....	10	..

TABLE IV. MISCIBILITY OF SULPHONATED CASTOR OR SULPHONATED OLIVE WITH OLIVE OIL

(Determined by amount of oleic acid required to clear)

Mixture *Parts*	Olive Oil *Parts*	Sulphonated Castor or Olive Oil	Oleic Acid to Clear: Sulph. castor oil mixture %	Oleic Acid to Clear: Sulph. olive oil mixture %
1	0.0	100	0	0
2	10	90	13	0
3	20	80	23	0
4	30	70	28	6
5	40	60	32	11
6	50	50	34	16
7	60	40	38	20
8	70	30	42	26
9	80	20	55	34
10	90	10	..	..

EFFECT OF ALKALI AND ALCOHOL

The concentrated sulphonated oils on the market usually contain a small amount of soap but a much greater quantity of free fatty acids. It was found that the completely neutralized oil is somewhat less soluble in mineral oils, but considerably less soluble in olive oil. This is shown, in Table V, by the amount of oleic acid necessary to clear the sulphonated-oil mixtures before and after neutralization. Alcohol[3] added to the neutralized oil reduces the amount of oleic acid by liquefying the soap, but an excess of alcohol has the opposite effect.

With mineral oils, there is an advantage in completely neutralizing the sulphonated oil, provided the proper amount of alcohol is also added, but not so with raw olive oil, since the large excess of oleic acid necessary to clear the mixtures, even in the presence of alcohol, renders the oil non-emulsifying.

TABLE V. EFFECT OF ALKALI ON THE MISCIBILITY OF SULPHONATED OLIVE AND RAW OLIVE OR MINERAL OIL

(Determined by amount of oleic acid to clear)

	Oleic Acid to Clear
Equal parts acid sulphonated olive and mineral oil	0
Equal parts neutralized sulphonated olive and mineral oil	2
Equal parts acid sulphonated olive and raw olive oil	12
Equal parts neutralized sulphonated olive and raw olive oil	34

LITERATURE CITED

[1] Bumcke, J. *Am. Leather Chem. Assocn.*, 22, 621 (1927).
[2] Geronazzo, *Boll. ufficiale staz. sper. ind. pelli mat. concianti*, 5, 416-20 (1927).
[3] Hart, *Ind. Eng. Chem.*, 21, 85 1929).

New Commercial Products From Cane Sugar

In a paper read before the Sugar Division of the American Chemical Society at New Orleans, on March 29, 1932, Drs. Gerald J. Cox and John Metschl, of Mellon Institute of Industrial Research, Pittsburgh, Pa., described some of their studies on materials made from sugar.

They have found that sucrose octa-acetate, which was first prepared in 1865, may find a useful place in modern lacquers. It is a resinous material which, when compounded with other materials, serves as an adhesive. It has also been employed in treating paper. Sucrose benzoate, another compound of sugar that has been known for many years, may find similar uses.

When sugar is treated with hydrochloric acid at a temperature somewhat higher than that of boiling water, it is converted into acidic substances. One of these acids, levulinic acid, was made and studied forty years ago. When it is properly treated with alcohol, fragrant esters are produced that may find uses as solvents in many fields.

Oil Stains

(Continued from page 276)

TABLE III.—OIL CONSTANTS

(Supplied by the Anglo-American Oil Company Limited)

—	"A"	"B" Pale	"C" Spindle	"D" Spindle	"E"	"F"
Sp. gr. at 60° F.	880/5	890/5	890/5	879/81	895/900	865
Closed flash-point	345°F.	370°F.	380°F.	385°F.	390°F.	375°F.
Open flash-point	370°F.	390°F.	395°F.	405°F.	405°F.	395°F.
Redwood viscometer at 70° F.	220″	200″	315″	300″	395″	265″
Redwood viscometer at 140° F.	55″	52″	64″	64″	72″	62″
Cold Test.....	20/25°	0°	25/30°	25/30°	25/30°	20/25°

(Supplied by Stemco Limited)

	Marcol	250 L White Oil	Half White 382
Sp. gr. at 60° F.	0.8475	0.8722	0.8692
Closed flash-point	365°F.	365°F.	330°F.
Redwood viscometer at 70° F.	135″	225″	212″

change is not necessarily the same as oxidation of unsaturated fatty acids. The same applies to mineral oils; strong color change is accompanied by very small chemical change. It may reasonably be assumed that color change (staining) may be tested for in a manner quite different from oxidation of oils, which latter refers rather to the formation of sticky viscous compounds. It may be of interest to note that these viscous compounds show very little color change until they are saponified with caustic alkalis. The soaps and free fatty acids thus produced are dark-colored substances possessing strong coloring power. Staining appears to depend on the presence of compounds, generally slightly colored and fluorescent in ultra-violet radiation, which are rendered more intense in color by atmospheric influences or fluorescent compounds which on exposure to light become intensely colored when viewed by daylight.

New Liquid Resin

Development of a new liquid resin to be known under the name of Abalyn is announced by the Naval Stores Department of the Hercules Powder Company.

The new product is a resinous plasticizer for nitrocellulose lacquers and other products. The properties of Abalyn indicate that it will find a wide application in the manufacture of such products as clear interior lacquers for metal and wood, alkali-proof lacquers, leather lacquers, coatings for fabric and paper, non-drying inks, rubber cements, adhesives, waterproofing compositions, transparent paper and similar products.

Technical Notes from Foreign Sources

Halogenated Thio-indigos

German Patent No. 453,718 (16/XII/'27).—*I. G. Farben-Ind. A.-G.*—The parent substance is a 6-6'-dihalogen-4-4'-dimethyl-thio-indigo, which is further halogenated in any of the usual methods in use. The products are red-violet dyestuffs of good color-strength, and the dyeings are almost absolutely fast to washing, which is not true of most of the thio-indigo dyestuffs.—Three examples are given.

Hexa-substituted Thio-indigos

German Patent No. 455,882 (26/1/'28).—*I.G. Farben-Ind. A.-G.*—(*addition to German Patent No.* 453,718 *of* 26/I/'28).—The present additional patent consists in a specification of the further halogenation of tetra-substituted thio-indigos, as 6-6'-4-4'-tetra-halogen-, 6-6'-4-4'-tetra-methyl-, or 4 - 4' - dihalogen - 6 - 6' - diamethyl-thio-indigos. The 5-5'- positions are open to further substitution, the neighboring substituting groups have made entrance to halogen difficult. In one example here given, the material is dissolved cautiously in cold chlorsulphonic acid, a little halogen-carrier, as iodine or sulphur, added, and chlorine slowly passed in. The product so obtained dyes cotton in clear violet-red tones, and the other products mentioned are similar.

Vat Dyestuffs of the Perylene Series

German Patent No. 455,279 (12/I/'28).—*Felice Bensa.*—Substituted perlyenes, as halogenated or nitrated derivatives, are condensed with aromatic acids or their halogen derivatives, anhydrides, or salts, or preliminary condensation-products such as benzoylated halogenated perylenes, are internally condensed by the action of aluminium chloride (anhydrous) or similar condensing agents. In one example, a dibrom-perylene, ground up intimately, 1 part, with 10 parts of benzoic acid and 5 parts of sublimed aluminium chloride, are heated for 3-4 hours at 150°-170° C. The products (11 examples) dye cotton from the vat a fast red-violet, blue, blue-green, violet-black, brown, etc.—Isolation of the products from the melt consists merely in grinding up the mixture with dilute HCl, filtering, washing, and drying.

Sulphur Dyestuffs—Perylene Series

German Patent No. 454,912 (29/XII/'27).—*Felice Bensa.*—Consists in heating perylene, simple or substituted, with sulphurizing agents, such as phosphorus trisulphide or pentasulphide, in presence or absence of diluting agents (solid, such as infusorial earth, to prevent caking together). The products dye wool or cotton in various tones—bright red, bright blue, etc.

Vat Dyestuffs—Perylene Series

German Patent No. 461,504 (31/V/'28). — *Felice Bensa.*—Benzoyl derivatives of dihydroxy-perylenes are heated with anhydrous aluminium chloride. In the one example given, the product forms an ultramarine blue vat, which dyes cotton the same color; after oxidation, the dyeing is a fine, somewhat greenish blue.

Vat Dyestuffs

German Patent No. 456,236 (2/II'28/).—*I.G. Farben-Ind. A.-G.*—In the original patent, the di-anhydride of 1-4-5-8-naphthalene-tetracarbonic acid, or the acid itself, is condensed with o-diamines, or their salts, in presence or absence of solvents or diluting agents. In this case, the tetra-acid or its anhydride is first condensed with o-nitro-amines, and the nitro-group of the condensation-product reduced. As reduction takes place, the final ring-closing to the imidazol derivative follows.

Testing Light-Fastness of Dyeings

Dr. H. Sommer—Monats. f. Textil-Ind. 287,46 (1931)—The fourth and last section of a series of papers, the previous one of which was abstracted at some length in these columns. The present section is devoted principally to a consideration of various light-sources, with a resume of the whole series of papers.

The need for some adequate source of powerful artificial "fading" light is due to both the relative weakness and the uncertain availability of sunlight during the greater part of the year (and it should be remembered that for northern Europe the winters are longer and darker than ours, on account of the higher latitude); and a considerable number of such illuminants, all of electrical nature, of course, has been tried out and variously reported upon during recent years. Dr. Sommer lays down three requisites for the ideal light-source:—

a—qualitative—it must give out a radiation essentially of the same nature as that of sunlight, and must possess a considerable similarity of the spectral energy-division of the solar spectrum.

b—quantitative—it must possess great intensity, so as to allow shorter exposures than are possible with sunlight even under favorable conditions.

c—cost—the power-consumption must not be unreasonable, nor must any other factors of unusual expense be involved.

No artificial light-source can, as far as we at present know, exactly replace sunlight, as far as the spectral values are concerned (i.e., active wave-length emission); the carbon arc and the tungsten glow-lamp come nearest to the requirements. Exact testing of promising light-sources gave the following results:—

a—Mercury-vapor arc (quartz-lamp)—this source has given very satisfactory results indeed, in studies of the fading of tinted paper (Dalen and Wilke, Papier-Fabr. 1928, 199), in comparison with sunlight; but the case is not so with the fading of dyed textiles. Most noteworthy is the considerably greater black-content of the swatches faded with this light-source, and the difference in rate of fading in various cases, so that the values, plotted on the psychological color-triangle, show considerable differences as compared to the normal (sunlight) values. Correspondingly, the calculated coefficients of fading show considerable differences as compared to the normal values. The author has calculated, from these coefficients, the relative intensity of the mercury arc as against sunlight, and finds that with cotton type-dyeings the average comparative values is 240%, for the wool type-dyeings an average of 120%, and with Victoria Blue paper 200%, as against 100% for sunlight. One hour's fading with the mercury arc corresponds roughly to two normal fading-hours, but the value is not constant for all dyeings. There exist discrepancies not only between the cotton and wool type-dyeings as classes, but within these classes also there is a lack of uniformity in value. The substratum (fiber) apparently plays an important part in the progress of the course of fading.

In the tests carried out with the mercury arc, which emits comparatively little heat, the swatches were exposed at a distance of 16 cm. from the source, temperature 30° C., relative humidity 40% (lamp burning for about 50 hours before beginning the tests, to allow reaching the point of uniform radiation, as the arc fluctuates seriously in its radiation during the first stage of use). In the tests with the following light-sources, which gave off relatively much heat, the swatches were exposed within an airtight exposure-case, faced with "UV-new" glass; within the case a "fan" (Fluegel—a one-blade affair?), kept in rapid motion, provided against stagnation of the enclosed air, and in addition air was led in under slight pressure at one side of the case, and a slight exhaust maintained at a vent on the other side, so that thorough cooling was provided for. The relative humidity was roughly imparted through a calcium chloride solution, and could easily be regulated by switching in or out, in the entering air-line, calcium chloride tubes for drying, and washbottles containing water, for humidifying the air as it entered. With this apparatus, these types of light-source were tested:—

b—Carbon arc-lamp; double flame arc-lamps of 6,000 HK light-energy were used with special carbons; the white-flame carbons, prepared with tungsten salts, whose light is comparable with that of sunlight (normal summer) in level countries, and the ultra-carbons, prepared with tungsten and iron salts, whose light is comparable to that of sunlight in high mountain altitudes; their UV radiation was about 10%.

On account of the heat given off by the arc, the distance of the samples to be exposed was increased to 50 cm.; the average temperature at that distance was 41° C., and the relative humidity 60%. The series of exposures was terminated after 70 hours, an account of the trouble of being obliged to renew the carbons so frequently, the great variation in the strength of the light, and the cost of current. It was found that a normal fading-hour corresponded to about 15 hours exposure with the white flame, and 9 hours with the ultra, arc. The fading effect appeared to be similar to that of sunlight.

c—Osram Point-light (Type 700 watt) — Hochheim and Knebel (Mell. Textil-Ber. 1925, 912) have obtained good results with this source, claiming that a 178-hour exposure at a distance of 15 cm. corresponds to a 12-day exposure in September sunlight. The author's work showed that at a distance of 30 cm. (necessary on account of the heat emitted), about 30 hours' exposure equalled one normal fading-hour. It was concluded that the relatively high cost of the lamp and its comparatively short life would make it out of the question for the present purpose, though its spectrum is so nearly like that of the sun's light that a better and cheaper form might be of great value.

d—Osram Vitalux (500 watt)—This lamp was tested, apparently, more exhaustively. Its bulb consists of a glass which permits the passage of the ultra-violet rays, so that the radiation in this region up to 2,700 Angstroems, and in the region from 2,900 to 3,200 Angstroems (0.04% of the total radiation) is as effective as the same components in sunlight. With sunlight, however, the ultra-violet component of long wavelength is stronger, and the maximum energy lies in the blue region, while with the Osram lamp the maximum lies in the infra-red; so that there is a distinct difference in effect, though this is less than with the other light-sources studied.

Two forms of the lamp were used, one with colorless, transparent bulb, without reflector, and a "silk-matted" bulb of blue glass, with a chromium-plated parabolic reflector. The first form (distance of swatches 30 cm.) proved to be rather weak in effect; 720 hours gave a degree of fading amounting to about 70 normal fading-hours (cotton), 10 (wool), and 16 (Victoria Blue paper). The second form of light-source proved to be more powerful, with the disadvantage that the heat as well as the light was concentrated by the mirror. Comparison with the effect of sunlight gave an average of 31% intensity for cotton dyeings, 8% for wool dyeings, and 24% for Victoria Blue paper; so that a normal fading-hour corresponded to perhaps 4 hours of exposure with the lamp. Again, however, the difference in effect upon wool and upon cotton dyeings showed this type of lamp to be not a real substitute for sunlight. The life of the lamp, too is only about 300 hours, and the intensity of the radiation is gradually cut down by the darkening of the bulb by deposition of the filament-material upon the inside of the bulb.

In other words, there is as yet no really effective substitute for sunlight.

The author adds a note regarding the Victoria Blue

used in the preparation of the test paper mentioned; that Krais, who originated this method of measurement, employs Victoria Blue B, not R; but that he himself, nevertheless, used the R brand, with equally good results; and that tests have shown the existence of still other dyestuffs which could be used just as well.

Newer Sulphonic Acids as Assistants in Textile Work

Dr. A. Bresser—Textil-Chemiker u. Colorist 137,11 (1930) (*Deutscher Faerber-Ztg. supplement*)—The modern search for new sulphonation-products, for use as wetting-out agents, emulsifying, and dispersive agents, has proceeded in part along well-known lines, by use of already known methods, and partly along newer lines, which give rise to products of entirely different nature (as far as the use of such products concerns the textile industry).

Aromatic sulphonic acids can of course be condensed with aliphatic alcohols, by means of suitable condensing agents, to form "alkylated sulphonic acids" (esters). Only the higher alcohols, from propyl alcohol onward (but this is hardly a higher alcohol) have been much employed, though attempts have been made to utilize methyl and ethyl alcohols. Little of value has resulted from such methods, as yet.

When at least two mols. of chlorsulphonic acid are allowed to react in the cold upon a mixture of an aromatic hydrocarbon and either methyl or ethyl alcohol, condensation takes place, with sulphonation, at the same time, of the hydrocarbon in the nucleus (oleum has the same action). If, for example, a mixture of 46 parts by weight of ethyl alcohol and 128 parts of naphthalene is treated gradually with 300 parts of chlorsulphonic acid at 70° C., and the temperature then raised to 130° for a short time, the product obtained forms a yellow-brown, water-soluble compound, which is also soluble in moderately dilute acids. Its solutions display a strong tendency to foam-formation, and so it is a valuable wetting-out and emulsifying agent. If tetrahydronaphthalene is substituted for the naphthalene, a product of similar properties is obtained, whose sodium salt is a soaplike, yellowish product, easily soluble in water, forming solutions of properties and value similar to the above.

Another group of substances is derived from unsaturated higher fatty acids, which are first saturated in the unsaturated linkage by introduction of an aralkyl radical (heating with an aralkyl halogenide, as benzyl chloride, in presence of a catlyst). Such a condensation-product is then sulphonated, doubtless in the aryl radical. For example, such an intermediate is produced by heating 282 parts of oleic acid, 253 parts of benzyl chloride, and 5 parts of anhydrous zinc chloride, to 150° C., the reaction proceeding to an end at this temperature, with evolution of HCl gas. This reaction requires about two hours. Of this product, 50 parts are sulphonated at the ordinary temperature with 30 parts of chlorsulphonic acid. When the mixture is diluted by pouring upon 60 parts of ice, two layers form, the lower one consisting of sulphonic acid; the upper layer is dissolved in 400 parts of water, and cleared of any cloudiness possibly present by extraction with ether (this would be satisfactory for small-scale work; on the large scale, some more safe solvent would be employed). It is then neutralized with caustic soda liquor, and evaporated, thereby yielding a yellowish powder, easily soluble in water, and not precipitable with common salt, though it is thrown down by acetic or moderately dilute mineral acids.

This sort of process has also been employed with some glycerides of fatty acids; for example, rape oil is benzylated as before, and the product sulphonated, in this case with chlorsulphonic acid diluted with monohydrate. Such products are not precipitated from aqueous solutions by acetic acid (at least, in reasonable amounts.)

Another line of work followed out consists in condensing the higher alcohols, from propyl alcohol onward, with aromatic sulphonic acids which are not derived from aralkylated poly-nuclear hydrocarbons. Such compounds contain the alkyl radical of the alcohol attached to the aromatic nucleus, and these substituted in such positions once or perhaps several times. The same, or similar, products can also be obtained by starting with the sulphonated aromatic hydrocarbon, and condensing this with the alcohol by means of sulphuric acid of suitable strength and temperature. In one way or another one arrives at a propyl—, or butyl—, or alkyl—naphthalene—sulphonic acid, which can be isolated easily, as, for example, the sodium salt, which is easily soluble in water, and possesses strongly dispersive power. Such substances are useful as they are, or they make possible, as emulsifying agents, the preparation of stable emulsions or colloidal solutions of hydrogenated aromatic hydrocarbons, very useful as assistants to soaps for cleansing or scouring.

Vat Dyestuffs Containing Sulphur (Indigoid)

German Patent No. 452,575 (14/XI/'27)—*Addition to G. P. No.* 445,218 (26/X/'24—*Leopold Cassalla and Co.*—1-8-Naphthoxyene-thiophene and derivatives of it, other than those mentioned in the principal patent, or in the subsequent additional patent No. 451,549, are condensed, as in the original patent, with alpha-isatine-derivatives (isatine arylides or chlorides) of the benzene or naphthalene series, or with their substitution products. The resulting compounds are similar in general to those of the original patent; blue to pure green dyestuffs, which differ, however, from the earlier homologues in being much faster to chlorine.

Vat Dyestuffs (Perylene Series)

German Patent No. 451,123 (21/X/'27)—*Felice Bensa of Genoa.*—Like certain other patented processes in the perylene group, this present one is simple; consisting in the nitration of perylene-quinone or mono-nitroperylene-quinone. The product, a dinitro-perylene-quinone,

dyes cotton from the vat much like the mono-nitro-product, but the dyeings are much purer and deeper in tone. The product, dyeing cotton violet, can be used as a dyestuff, or as an intermediate for further syntheses in the series.

Vat Dyestuffs (Benzanthronyl Series)

German Patent No. 453,135 (29/XI/'27)—*I. G. Farben-Ind. A.G.*—Halogenated derivatives of benzanthronyl mercaptans, sulphides, or disulphides, or their derivatives, are condensed with amines; or the amino-derivatives of benzanthronyl mercaptans, sulphides, or disulphides, or their derivatives, are condensed with compounds containing reactive halogen; and the products are treated with alkaline condensing agents, soda, sodium acetate, etc., or with catalysts such as copper powder. The products have the general formula R-NH-benzanthronyl-S-R', R and R', being aliphatic or aromatic, substituted or unsubstituted, radicals. The products are vat dyestuffs dyeing, in the 8 examples given, red-brown, blue-gray, violet-blue, merino-blue, green-blue, neutral gray.

Vat Dyestuffs (Anthraquinone Series)

German Patent No. 450,921 (18/X/'27)—*I. G. Farben-Ind. A.G.*—In German Patent No. 237,236, and in the supplementary patents Nos. 237,237 and 248,170, 1-nitro- or 1-chlor-anthraquinone-2-carbonic acids are condensed with arylamines to aryl- 1-amino-anthraquinone-carbonic acids, and these, by elimination of water, into the derived acridones. The present patent covers the compression of these two steps into one operation, catalysts or condensing agents not being necessary, though very advisable for convenience; essentially the components are heated to a sufficient temperature in a suitable medium. Five examples are given. The process covers a new method, rather than necessarily new products; e.g., example 1 of this patent yields a dyestuff identical with that of example 4 of Patent No. 237,236.

Azo Dyestuffs

German Patent No. 461,499 (31/V/'28)—*I. G. Farben-Ind. A.-G.*—3-Nitro-4-diazo-1-phenol ethers are coupled with acetacetic anilides, containing in the ring an alkyl group in the ortho, or an alkoxy group in the para, position to the amino group which has formed the anilide grouping. The products are reddish-yellow dyestuffs, whose lakes are very fast toward light. Among the anilides mentioned in the three examples given are acetacetic o-toluide and acetacetic p-anisiде.

Dyed Textiles: Determination of Fastness to Light

H. Sommer. Leipzig. Monats. Text. Ind., 1931, 46, 25-28, 64-66, 99-102, 134-135, 177-179, 215-217, 250-253, and 287-289.

The author deals first with the effect of source of light, atmospheric conditions and duration of illumination, the practical difficulties of judging fading subjectively by comparison with the Fastness Commission's standard types, the importance of replacing such subjective methods by objective methods, and the progress represented by the "degree of fading" method of Ziersch and the "half value time of fading" of Jost and Flütsch. The adoption of objective methods demands more uniform conditions of test than hitherto and in order that reproducible results may be obtained the following standard conditions of exposure are proposed. The test pieces shall be exposed out of doors in a box allowing free access of air and atmosphere moisture and having a cover of U-V New Glass 2 mm. thick. The box shall be arranged east to west and inclined at an angle of 45° so that the test samples face directly south. Krais' Victoria Blue paper, exposed under the same conditions as the test samples, is a suitable means of determining the number of hours of illumination if the paper is prepared under standard conditions and standardized with reference to a particular place. Only under these conditions are the degree of fading values and half value times of fading obtained at different places comparable. Accordingly, a "standard fading hour" curve has been prepared by making careful measurements with Victoria Blue paper of the intensity of sunlight at Berlin-Dahlem over a period of one year. With the aid of this curve the "standard fading hours" of paper illuminated at any other place can be evaluated from step photometer measurements, and a formula is also given for calculating the life of a color at a given place from the half value time of fading, referred to standard fading hours, and the fading coefficient for Victoria Blue paper for the summer months at that place. The author next deals with the practical difficulties of the Ziersch and Jost and Flütsch methods, namely, that in the former a definite number of standard fading hours must be accurately achieved, while in the latter very long periods of exposure are necessary, and shows how these difficulties may be overcome by the use of the general fading formula $A = n\sqrt{t}$ in which A is the percentage degree of fading, t the number of active "standard fading hours" and n the fading coefficient of the dyeing. The fading coefficient is an absolute value for the fastness of a dyeing independent of the period of illumination and from which the half value time of fading can be calculated. It bears a definite relationship to depth of color expressed by $n = N(\log c - \log f)$, in which the fading constant N is characteristic for the behavior of the dye in all depths of shade on the same substrate. (The work described in this section of the paper has been dealt with in a previous abstract.) The relationship between fading coefficient and degree of fading, period of illumination and depth of color makes it possible to standardize degrees of fastness to light, and preliminary proposals are made on the basis of experiments on cotton and wool type dyeings of the Fastness Commission for the establishment of six fastness classes. Finally, experiments with a number of sources of artificial light have shown that none of these can replace sunlight in testing for fastness to light.—*Journal Textile Institute.*

NEW PATENTS

Abstracted by Synthetic Organic Chemical Mfrs. Assn.

Production of Vat Dyestuffs. (Halogeniferous ms-anthradianthrones. A division of above Patent No. 1,-841,961.) Max Albert Kunz, of Mannheim, and Karl Koberle, of Ludwigshafen-on-the-Rhine, Ger., assignors to General Aniline Wks., Inc., of N. Y., N. Y., No. 1,841,963, January 19, 1932.

Production of Vat Dyestuffs. (Comprises subjecting on allo-ms-naphthodianthrone in acid solution to the action of an oxidizing agent. A division of above Patent No. 1,841,961.) Max Albert Kunz, of Mannheim, and Karl Koberle, of Ludwigshafen-on-the-Rhine, Ger., assignors to General Aniline Wks., Inc., of N. Y., N. Y., No. 1,841,964, January 19, 1932.

Production of Vat Dyestuffs. (Comprises subjecting an allo-ms-naphthodianthrone to halogenation and simultaneous condensation. A continuation in part of above Patent No. 1,841,961.) Max Albert Kunz of Mannheim, and Karl Koberle, of Ludwigshafen-on-the-Rhine, Ger., assignors to General Aniline Wks., Inc., of N. Y., N. Y., No. 1,841,965, January 19, 1932.

Azo-Dyestuffs and Process of Making Same. (Obtained by diazotizing paratoluenesulfonic acid ester of 1:8-amino-naphthol-3:6-disulfonic acid and coupling the diazo-compound with cresidine and treating with phosgene in alkaline solution; dye vegetable fiber orange, red, brown and violet tints fast to light). Guillaume de Montmollin, Hans Cubler, and Joseph Spieler, of Basel, Switzerland, assignors to Society of Chemical Industry in Basle, of Basel, Switzerland, No. 1,846,546, February 23, 1932.

STATEMENT OF THE OWNERSHIP, MANAGEMENT, CIRCULATION, ETC., REQUIRED BY THE ACT OF CONGRESS OF AUGUST 24, 1912, OF AMERICAN DYESTUFF REPORTER, published bi-monthly at New York, N. Y., for April 1, 1932.

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Before me, a Notary Public in and for the State and county aforesaid, personally appeared Alfred P. Howes, who, having been duly sworn according to law, deposes and says that he is the Publisher of the AMERICAN DYESTUFF REPORTER, and that the following is, to the best of his knowledge and belief, a true statement of the ownership, management (and if a daily paper, the circulation), etc., of the aforesaid publication for the date shown in the above caption, required by the Act of August 24, 1912, embodied in section 411, Postal Laws and Regulations, printed on the reverse of this form, to wit:

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4. That the two paragraphs next above, giving the names of the owners, stockholders, and security holders, if any, contain not only the list of stockholders and security holders as they appear upon the books of the company but also, in cases where the stockholder or security holder appears upon the books of the company as trustee or in any other fiduciary relation, the name of the person or corporation for whom such trustee is acting, is given; also that the said two paragraphs contain statements embracing affiant's full knowledge and belief as to the circumstances and conditions under which stockholders and security holders who do not appear upon the books of the company as trustees, hold stock and securities in a capacity other than that of a bona fide owner; and this affiant has no reason to believe that any other person, association, or corporation has any interest direct or indirect in the said stock, bonds, or other securities than as so stated by him.

5. That the average number of copies of each issue of this publication sold or distributed, through the mails or otherwise, to paid subscribers during the six months preceding the date shown above is.....(This information is required from daily publications only.)

ALFRED P. HOWES, Publisher

Sworn to and subscribed before me this 29th day of March, 1932.
(SEAL) CAROLINE ESSENBREIS
(My commission expires March 30th, 1933.)

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"Water Filters and Filtration Equipment" is the title of a new, 28-page bulletin describing the principles of filtration, the pretreatment of different classes of waters, the various types of chemical feeds, vertical and horizontal pressure filters, concrete and wood gravity filters, activated carbon filters, etc., published by the Permutit Company, 440 Fourth Avenue, New York. Copies are free on request.

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